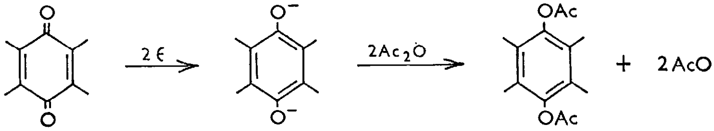
75. *Investigation of Carbonyl Groups in Solvent Extracts of Coals.*

By P. H. GIVEN and M. E. PEOVER.

Solvent extracts of coals have been reductively acetylated in dimethylformamide solution by electrolysis at a controlled potential and addition of ^{14}C-labelled acetic anhydride. The variation of acetyl uptake with controlled potential indicates that most of the carbonyl groups are reduced in a range of potential where known quinones and certain highly conjugated aromatic ketones are reduced. The significance of the numerical results is discussed in relation to the interpretation of the infrared spectra of the materials. It is concluded that the most probable carbonyl contents are in the range 1—2·5% of O as $>C=O$, the proportion increasing slowly as the carbon content of the parent coal decreases. About 80—90% of the oxygen in the extracts can now be accounted for as carbonyl plus hydroxyl.

THE presence of strongly conjugated carbonyl groups, probably quinonoid, in solvent extracts of coals has been inferred from the infrared spectra of material before and after reductive acetylation,[1] and from polarographic studies.[2] The amounts of these groups have been estimated from the quantity of electricity consumed in controlled potential electrolysis of solvent extracts in dimethylformamide,[3] by selecting a potential at which one would expect all the carbonyl groups but no others to be reduced. There are reasons [3] for supposing that this discrimination would be obtained at a controlled potential of —1 v *vs* mercury pool reference electrode, but the choice is still somewhat arbitrary. We have therefore explored a method of estimation that does not require any such choice. The hydroxyl groups in solvent extracts of coals are acetylated, and the products reduced electrolytically as before; then ^{14}C-labelled acetic anhydride is added, and the acetyl content of the product determined from its radioactivity. We have previously shown [4] that in dimethylformamide quinones are reduced to the quinol di-ions which remain unprotonated in anhydrous solvents and react rapidly with acetic anhydride in the cold:



This method enabled us to study the reduction of carbonyl groups as a function of controlled potential and thus to gain some qualitative indications of their nature. However, as will be shown below, the precise significance of the values of the " carbonyl contents " obtained is not entirely clear.

EXPERIMENTAL

The materials and method of electrolysis have been described previously.[3] Tetraethylammonium iodide was used as supporting electrolyte. Acetic anhydride was purified by the method of Walton and Withrow.[5] The electrolytic cell, also described previously,[3] employed a stirred mercury cathode and a silver anode; a small pool of mercury in supporting electrolyte solution, separated from the bulk of the liquid by a porous glass disc, served as a reference electrode. The quantity of electricity used was measured with a hydrogen–oxygen coulometer.[6]

The solvent extracts were prepared by Soxhlet-extraction from standard samples of five highly vitrainous low-ash coals, designated DO, DIII, DVI, DIX, DXIII (for full details of the

---

[1] Brown and Wyss, *Chem. and Ind.*, 1955, 1118.

[2] Given and Schoen, *J.*, 1958, 2680.

[3] Given and Peover, Proc. Inst. Fuel Conf., " Science in the Use of Coal," 1958, Paper 2, p. A-33.

[4] Given, Peover, and Schoen, *J.*, 1958, 2674.

[5] Walton and Withrow, *J. Amer. Chem. Soc.*, 1923, **45**, 2689.

[6] Lingane, *ibid.*, 1945, **67**, 1916.

coals see ref. 3; their carbon contents were 77·7, 81·1, 83·9, 86·0, 89·2% dry, ash-free). Some of the extracts were not completely soluble in dimethylformamide; where this was so the soluble part only was taken for the experiments, and the figures for % extraction in Table 1 represent this part as a fraction by weight of the original coal. The entry in Table 1 " DMF-1-naphthol " signifies the dimethyl formamide-soluble part of the naphthol extract.

TABLE 1. *Carbonyl number of solvent extracts of coals.*

Run no.	Coal	Extracting solvent *	Extractn. (%)	Prior treatment [a]	Reduction pot. (v)	O (%) in the extract	O (%) reacting as OH in the pretreatment [b]	O (%) as C=O from coulometry [c]	O (%) equiv. to [^{14}C]Ac uptake	Found (% of ash-free extract)			
										C	H	N	S
1	DO	DMF	2·5	AcCl	−0·8	14·0	2·4	2·5	3·0	77·6	6·0	2·1	1·5
2				AcCl	−1·0	14·0	2·4	4·3	3·8				
3				HMDS	−1·0	14·0	6·5	5·4	4·45				
4				AcCl	−1·4	14·0	2·4	7·7	4·5				
5	Scottish vitrain	DMF–1-naphthol	90	AcCl	−1·2	11·4	3·0	3·7	4·0	82·0	4·9	1·1	0·5
6	DIII	DMF–1-naphthol	80	AcCl	−1·0	10·0	3·8	3·0	2·8	82·3	5·0	1·4	0·8
7		Pyridine (*a*)	18	„	−0·7	9·0	2·5	1·9	1·5	82·5	5·5	2·1	0·6
8				„	−1·0	9·0	2·5	4·1	3·2				
9				„	−1·2	9·0	2·5	4·7	3·75				
10				„	−1·4	9·0	2·5	6·8	4·2				
11				AcCl–Ac$_2$O	−1·4	9·0	4·2	6·8	4·2				
12		(*b*)		Ac$_2$O	−1·4	9·2	4·7	7·9	4·0	81·8	5·8	2·2	1·0
13		DMF (*a*)	3	AcCl	−1·0	9·9	4·3	4·4	3·5	82·3	6·2	1·0	0·6
14		(*b*)	12	—	−1·4	9·6	4·9 [d]	—	4·0	82·5	6·2	1·1	0·6
15		Butanone	3	AcCl	−1·0	9·2	3·6	4·0	3·65	81·7	6·7	1·8	1·0
16				„	−1·4	9·2	3·6	—	4·1				
17	DVI	DMF	7·5	AcCl	−1·0	7·4	2·5	3·0	3·0	83·3	6·1	2·2	0·8
18				AcCl–HMDS	−1·0	7·4	>2·5	—	3·2				
19	DIX	DMF–1-naphthol	90	AcCl	−1·4	7·5	1·8	—	2·2	83·6	5·2	2·0	1·0
20		DMF–pyridine	8	AcCl–Ac$_2$O	−1·0	6·0	2·6	3·2	1·9	85·2	6·0	2·3	0·6
21				„	−1·4	6·0	2·6	9·0	2·8				
22		DMF	18	Ac$_2$O	−1·4	6·5	2·8	—	3·3	84·5	5·5	2·4	1·3
23	DXIII	DMF (*a*)	3	AcCl–	−1·0	4·4	1·4	—	1·8	85·9	5·9	2·2	0·9
24				AcCl–Ac$_2$O	−1·4	4·4	1·4	4·4	1·8				
25		(*b*)	8	Ac$_2$O	−1·4	3·3	1·2	—	1·8	88·7	5·8	1·2	0·9

[a] HMDS = reaction with hexamethyldisilazane to give trimethylsilyl ether. [b] See text. [c] C=O assumed to be quinonoid. [d] Determined radiochemically; see text. * DMF = dimethylformamide.

Two methods were used for the preliminary acetylation: the solvent extracts were refluxed with excess of acetyl chloride for 6 hr. or with acetic anhydride in pyridine for 24 hr. The products were washed with water and dried. In a few cases the hydroxyl groups were not acetylated, but were converted into their trimethylsilyl ethers by treatment with hexamethyldisilazane and trimethylchlorosilane in pyridine: $ROH + (Me_3Si)_2NH = RO{\cdot}SiMe_3 + Me_3Si{\cdot}NH_2$.

About 0·5 g. of treated coal extract in 100—250 ml. of dimethylformamide was taken for each experiment.

The labelled acetic anhydride had a specific activity of about 5 mc/mole. 1·4 ml. (*i.e.*, 500% excess) per g. of coal extract was added at the end of the electrolysis, and the mixture was left overnight under oxygen-free nitrogen.

The solution was filtered into an equal volume of water, and the resulting precipitate filtered off, washed with water, 10% acetic acid, and water, and then dried to constant count rate in a vacuum-desiccator over alumina. The dried sample was placed in an aluminium tray to a depth greater than " infinite thickness " for the energy of the radiation emitted by ^{14}C (*i.e.*, 5 mg./sq. cm.). A thin mica end-window tube was used with a standard scaling unit. The tray was placed at a fixed distance from the end-window great enough to ensure that small variations in the depth of the bed of sample did not affect the count rate. Counting was continued till about 10,000 had been recorded. The count rate was 2000—8900 min.$^{-1}$.

The calibration factor relating count rate and [^{14}C]acetyl content was determined by observing the count rates of purified samples of acetanilide and 2-naphthyl acetate (prepared by acetylation of aniline and 2-naphthol respectively with labelled anhydride). The two values of the factor thus obtained agreed within 1%, the experimental error in the counting technique.

RESULTS

The numerical results are collected in Table 1.

In control experiments acetylated but unreduced materials were treated in dimethylformamide with labelled anhydride. The count rate of the products, worked up as above, was about 90 min.$^{-1}$ compared with 2000—8000 min.$^{-1}$ when the material was reduced. This low value shows that neither adsorption of [^{14}C]acetic acid nor ester exchange with inactive acetyl was significant. About 90% of the activity was removed by hydrolysis of one of the products in boiling 12M-sulphuric acid for 2 hr.

A further check on the method was provided by experiment 14 (see Table 1), in which the total amount of oxygen in an extract, as OH + CO, was determined by employing ^{14}C-labelled reagent for both the preliminary and the reductive acetylation. To ensure that all hydroxyl had reacted the product was further treated with acetic anhydride in pyridine at 100° after the reductive acetylation step. The full results (%) were:

Total O	9·6	hence	O as CO, by difference	4·4
Total O as OH + CO	9·3	whereas	O as CO, direct detn. as above	4·0
O as OH (radiochemical Ac detn.)	4·9			

Over 95% of the activity of the fully acetylated material was removed by hydrolysis. The results prove that the carbonyl determinations are not affected by ester-exchange, and that acetylatable hydroxyl is produced by reduction. It is clear, moreover, from the hydrolyses that no significant *C*-acetylation occurs after reduction, as is confirmed by the absence of a carbonyl band at 1670—1700 cm.$^{-1}$ in the spectra of the products.

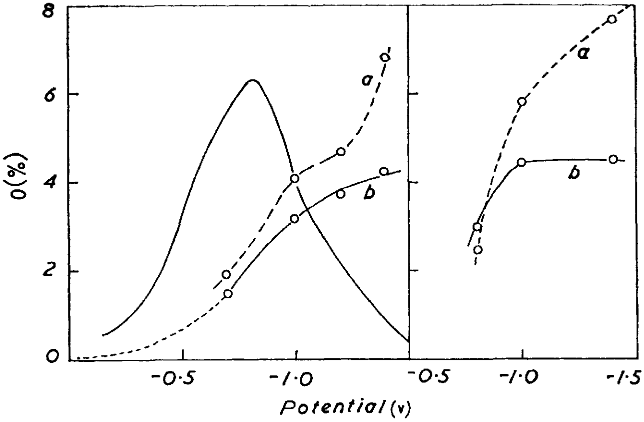
The analytical prodecure has been applied to a few known compounds; results over 90% of the theoretical were obtained with anthraquinone and naphtha-1,4-quinone, and in a preparative experiment 1,4-dihydroxyanthraquinone afforded a 94% yield of 1,4,9,10-tetra-acetoxyanthracene. However, benzophenone and benzanthrone had apparent carbonyl contents (by the radiochemical method) only about 30% of the true values, presumably because their reduction yields the alcohols rather than the alkoxide ions.

DISCUSSION

In what follows the carbonyl content equivalent to the measured uptake of labelled acetyl after reduction will be referred to as the radiochemical " carbonyl number," and the content of carbonyl, assumed to be entirely quinonoid, equivalent to the electricity consumed as the coulometric carbonyl number: if the carbonyl were ketonic (*i.e.*, 2 electrons per oxygen atom required for reduction) the coulometric figures would have to be halved. These coulometric figures will include the electricity required for any reduction of other groups, such as aromatic nuclei; this effect is no doubt important at the more negative potentials, where the coulometric and radiochemical figures begin to diverge widely. The variation of the carbonyl numbers with reduction potential, rank of coal, etc., will be discussed first and the absolute significance of the numbers considered later.

Some of the carbonyl numbers are plotted in Figs. 1 and 2 against reduction potential. It will be seen from these and Table 1 that the radiochemical values have reached a fairly well-defined limit by —1 v or in some cases —1·4 v, while the coulometric values increase without apparent limit. Previous evidence for the presence of carbonyl groups in solvent extracts of coals has been based on the existence of a polarographic diffusion current in a region of potential where quinones are the only likely substances to be reduced,[2,3] and on the change in infrared spectrum on reductive acetylation.[1] This evidence is not unequivocal and was not universally accepted. However, the present observations, that a further uptake of hydrolysable acetyl groups is made possible by reduction in a limited range of potentials, provides unequivocal qualitative evidence that carbonyl groups are present. The possibility that this uptake is due to exchange reactions has been excluded.

FIG. 1. FIG. 2.



Variation of carbonyl number with reduction potential for (FIG. 1) *a pyridine extract of coal* DIII *and* (FIG. 2) *a dimethylformamide extract of coal* DO.

(*a*) O (%) *as* C=O, *assumed quinonoid, from coulometry.* (*b*) O (%) *equivalent to* [^{14}C]*acetyl uptake. The potential is the controlled potential* (v) *of reduction* vs *a mercury pool reference electrode. The peaked curve in Fig.* 1 *is an approximate distribution curve for radiochemical carbonyl number with potential.*

It will be noted that treatment with acetyl chloride is an inefficient method of acetylating the hydroxyl groups in some extracts (compare OH figures in runs 2 and 3, 10 and 11, 17 and 18; contrast these with 23 and 24). Unfortunately the acetyl determinations, which showed this inefficiency, were not available until most of the electrolyses had been completed. Acetic anhydride–pyridine and hexamethyldisilazane are more reliable. In the remainder of the work either both methods of acetylation were applied successively or the silazane was used. However, in a few cases it was shown by comparative experiments that hydroxyl unacetylated by acetyl chloride was too unreactive to be affected by acetic anhydride in the cold at the end of the electrolysis (compare runs 2 and 3, 10 and 11, 17 and 18). We therefore conclude that there is no reason for supposing that the carbonyl numbers in Table 1 are inaccurate because of the incompleteness of the preliminary acetylation. In the cases where the figures " % O reacting as OH in pretreatment " are too low, the percentages of total oxygen accounted for as OH + CO are minima; in calculating this total (see Table 3) the hydroxyl content from a reliable determination has been used whenever possible instead of the % OH reacting in the actual pretreatment.

The radiochemical results indicate that most of the carbonyl groups are reduced in the potential range 0 to —1·0 v; an approximate distribution curve for one particular extract is included in Fig. 1, which shows that about 50% of the groups are reduced in the narrower range —0·6 to —1·0 v; with some of the other extracts the proportion is considerably higher. Table 2, giving the half-wave potentials of some carbonyl compounds of known structure, measured under the same conditions used for the work with coal (electrolysis in 0·1N-tetraethylammonium iodide in dimethylformamide), shows that the second waves of most of the quinones listed and the first waves of certain highly conjugated ketones fall within the range of potentials in which a major fraction of the carbonyl groups in coals are reduced. It is also evident that simple aromatic ketones (such as benzophenone) account for only a small fraction of carbonyl groups in the coal extracts, and there is no evidence that any aliphatic ketonic groups are present.

TABLE 2. *Half-wave potentials of some carbonyl compounds.*

(Data from ref. 4; also preceding paper, and Wawzonek, Berkey, Blaha, and Runner, *J. Electrochem. Soc.*, 1956, **103**, 456).

Substance	$-E_{\frac{1}{2}}$ (v *vs* Hg pool in 0·1N-NEt$_4$I in dimethylformamide)
Benzoquinone	0·04,* 0·15
Naphtha-1,4-quinone	0·10, 0·76
Anthraquinone	0·32, 0·99
1,4-Dihydroxyanthraquinone	0·07, 0·58
Phenanthraquinone	0·12, 0·69
9,10-Dihydroxynaphthacene-11,12-quinone	0·23, 0·74
3,3′,5,5′-Tetramethylstilbenequinone	0·03, 0·16
3,3′,5,5′-Tetra-t-butylstilbenequinone	0·04, 0·30
Tetraphenylcyclopentadienone	0·33, 0·89
Benzanthrone	0·74, 1·38
Purpurogallin	0·92, 1·50
3,7,3′,4′-Tetra-acetoxyquercitin	0·93, 1·39
Quercitin	1·21, 1·93
Benzophenone	1·22, 1·50
Xanthone	1·15, 1·55

* In presence of coal extract as maximum suppressor.

The results in Table 1 show that the radiochemical carbonyl numbers fall slowly as the carbon content of the parent coal rises (compare runs 3, 5, 11, 17, 18, 23), and may also fall somewhat where the percentage extracted is high (see also Table 3). The carbonyl content of the whole coal is presumably slightly less (0·1?) than that of a naphthol extract.

The view to be taken of the absolute significance of the carbonyl numbers depends to some extent on the interpretation of the infrared spectra of coals and their solvent extracts. The only band in the spectra of coals and extracts that could be associated with carbonyl is the intense one found at 1600 cm.$^{-1}$; the intensity of this band is higher than one would expect for an aromatic skeletal vibration, which in known aromatic compounds is found at the same frequency and is normally rather weak.[7] The assignment of a frequency as low as this to carbonyl requires that the groups are not only strongly conjugated but also chelated to hydroxyl (as in certain hydroxy-quinones and -flavones, and tropolones). (However, there are a few oxygen-containing compounds that have a strong band at 1600 cm.$^{-1}$ but are not hydroxyl-carbonyl chelated systems; examples are 3,3′,5,5′-tetra-t-butylstilbenequinone and the 2,4,6-tri-t-butylphenoxide radical. We are indebted to Drs. Wender and Friedman for this information and for the samples of the stilbenequinones, which enabled us to determine the half-wave potentials included in Table 2.)

---

[7] Brown, *J.*, 1955, 744; *Fuel*, 1959, **38**, 55.

The 1600 cm.$^{-1}$ band is not affected by acetylation of the coals or conversion into trimethylsilyl ethers. Hence, if the above assignment of the band is correct, the chelated hydroxyl group is resistant to these reactions before reduction of the carbonyl groups; this behaviour is unusual. After the breaking of chelation by reduction, however, all free hydroxyl must be acetylated, since no new hydroxyl band can be seen in the infrared spectra; moreover, if one had to assume an additional hydroxyl content equal to the carbonyl numbers in Table 1, the total amount of oxygen accounted for as OH + CO would greatly exceed the total actually present. Therefore, the true carbonyl contents must be one-half of the radiochemical carbonyl numbers, the other half representing the chelated hydroxyl (previous determinations of hydroxyl in coals are thus too low); the results at the most negative controlled potentials, calculated on this basis, are collected in Table 3.

TABLE 3. *Distribution of oxygen in solvent extracts of coals* (*carbonyl being assumed as chelated to unreactive hydroxyl*).

Coal	C (%) in coal	Extracting solvent †	O (%) as C=O	O (%) as OH (total) *	O (%) accounted for as C=O + OH
DO	77·7	DMF	2·25	8·75	78
Scottish vitrain		DMF–naphthol	2·0	>5·0	>61
DIII	81·1	,,	1·4	>5·2	>66
		Pyridine (*a*)	2·1	6·3	93
		(*b*)	2·0	6·7	95
		DMF (*b*)	2·0	6·9	93
		Butanone	2·05	>5·65	>84
DVI	83·9	DMF	1·6	>4·1	>77
DIX	86·0	DMF–naphthol	1·1	>2·9	>53
		DMF–pyridine	1·4	4·0	90
		DMF	1·65	4·45	94
DXIII	89·2	DMF (*a*)	0·9	2·3	73
		(*b*)	0·9	2·1	91

* Total of directly determined OH + chelated OH equal to C=O content. † DMF = dimethylformamide.

The above conclusion makes it necessary to suppose that most of the carbonyl groups are ketonic, that is, that the coulometric carbonyl numbers should also be halved: the discrepancy between the two sets of figures at potentials up to −1 v would then remain fairly small. As noted above, only a few ketonic compounds, with rather special structural features are reduced in the range of potentials observed for coal extracts.

In recent (unpublished) work, Drs. L. Blom of Geleen, Netherlands, has confirmed the presence of a chelated hydroxyl–carbonyl system in coals by the use of triacetylboron as a reagent specific for this kind of system. Such carbonyl contents as are available so far by this method are of the same order as those in Table 3. (We are indebted to Drs. Blom for this information and for permission to quote it in advance of publication.)

Only the above interpretation appears to reconcile most of our results, chemical and spectroscopic. However, it implies that all the carbonyl groups in coal extracts are present in a chelated system with hydroxyl, and that this system is of unusual properties. Moreover, one would expect on reductive acetylation of an acetylated extract a marked decrease in intensity of the band at 1600 cm.$^{-1}$ and a marked increase in the ester bands at 1760 and 1200 cm.$^{-1}$; but these changes, although observed, are weak.* The interpretation is not, therefore, wholly satisfactory, but there is no alternative apparent at present that does not ignore a substantial proportion of the results.

Analyses and chemical acetyl determinations were made by the Microanalytical Laboratory of this Association. The authors are indebted to Mr. R. F. Littlejohn for assistance with

---

* Brown and Wyss [1] found the intensity of the 1600 cm.$^{-1}$ band in the spectrum of an acetone extract of DIII coal to be reduced by about half on reductive acetylation. However, the extract represented only 2—3% of the whole coal; and their reduction system (zinc–acetic acid) probably reduced some aromatic nuclei as well as carbonyl—it is less selective than that used here.

radiochemical technique and to Dr. J. K. Brown for determinations of infrared spectra and discussions of their significance. The work was carried out in the Chemistry Department of the British Coal Utilisation Research Association, and is published by permission of the Association.

British Coal Utilisation Research Association,
Randall's Road, Leatherhead, Surrey.

[*Received, June 8th,* 1959.]