

Selective Chemical Reactions for the Study of Coal Macerals

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That the petrological classification of coal components in four main groups, known as vitrinite, exinite, micrinite and fusinite, has chemical and physical significance, as well as practical importance, is already established. There is petrographic and palaeobotanic evidence indicating that each of these groups is complex and that several varieties of each exist, but little chemical work has been carried out to supplement and consolidate this evidence. Such work is in progress in this laboratory; so far, attention has been paid mostly to the development of experimental techniques, but a start has been made in applying them to the study of vitrinite structure.

It is obvious that structural differences between two or more "vitrinoids"¹ found in the same coal will be more subtle than the differences between, say, vitrinite and exinite. A comparison of vitrinoids from different coals but of similar rank will also require subtle distinctions. If these distinctions can be established and understood, our understanding of the concepts of rank and metamorphosis should be strengthened considerably, and knowledge of the relation of constitution to behavior increased. Research of this kind clearly requires particularly sensitive techniques, and any chemical reactions used must be as selective and as informative as possible. In this paper the extension and improvement of two such chemical reaction techniques are described, together with their application to some purified vitrinitic materials.

Samples Studied.

In some of the preliminary experiments designed to elucidate the mechanism of the dehydrogenation reaction, a sample of vitrain from the Bruceton mine of the Pittsburgh seam was used. The elementary analysis is shown in Table 1; the petrographic analysis of a block from the same batch of coal is: vitrinite, 85%; semi-fusinite, 6%; fusinite, 2%; exinite, 4%; micrinite, 2%; and pyrite, 1%.

The other samples were pure vitrinites separated by float-and-sink techniques from the bright bands in selected vitrains. Their properties are collected in Table 1. Samples MP 10a and 10b were taken from different levels in one pillar section of the same seam, but differ appreciably in reflectance, and represent different vitrinoids in the classification of Schapiro and Gray.² Samples MP 11 and 17 have similar reflectances and represent the same vitrinoid V 9 according to Schapiro and Gray; they are, however, of quite different geological age and derived from different types of plant material, since MP 11 is an Appalachian coal laid down in the Pennsylvanian period of the Palaeozoic and MP 17 is younger, have been laid down in the Cretaceous period of the Mesozoic (ages approximately 300 and 120 x 10⁶ years respectively).

The hydroxyl contents of the samples are included in Table 1 for completeness; they are repeated from an earlier publication.³ It seems clear that samples MP 11 and 17 do differ somewhat in elementary analysis, but the carbon content of MP 17

may be somewhat too high*.

The infra-red spectra of all four vitrinites have been obtained. The spectra of MP 10a and 10b do not differ significantly, except that a difference of the intensity of the hydroxyl band at 3400 Å is observed, paralleling the hydroxyl contents determined chemically. The spectra of MP 11 and 17 also resemble one another closely; here again the hydroxyl bands differ in intensity, and the distribution of hydrogen between aromatic and aliphatic structures is evidently somewhat different (see Table 3 below).

Table 1. Analyses of Samples Studied

Sample No.	Source seam and location	Av. Reflec- tance in oil, %	Per cent d.a.f.					
			C	H	N	S	O*	O as OH
MP 10a	Lower Freeport West Sunbury, Pa.	0.743	82.6	5.4	1.6	1.4	9.0	5.6
MP 10b	Lower Freeport West Sunbury, Pa.	0.630	83.8	5.3	1.6	1.1	8.2	3.9
MP 11	Upper Freeport, Maysville, Pa.	0.995	84.9	5.2	1.5	0.8	7.6	3.2
MP 17	Frederick, Valdez, Colo.	0.934	86.6	5.5	1.9	0.8	5.2	2.0
-	Pittsburgh Bruceeton Vitrain	-	83.6	5.6	1.7	2.0	7.3	-

* by difference

Reduction with Lithium.

Lithium in aliphatic amines is a powerful reducing agent for aromatic systems, naphthalene, for example, being reduced to the octa- or deca-hydro derivative. The reaction proceeds, depending on the solvent, at 18 or 100°, and breakage of carbon-carbon bonds, such as occurs in catalytic hydrogenation, is not found. Both ethylamine⁴ and ethylene diamine^{5,6} have been used as the amine component in the application of the reaction to coals; the latter causes somewhat more extensive reduction of the coal, but is much more toxic and is impossible to remove completely from the coal after reaction. The extent of reduction varies strongly with rank, passing through a sharp maximum with vitrains of about 89% carbon content.^{4,5} The solubility of the coal in pyridine is always increased by the reaction, and the magnitude of the increase varies with rank in a manner closely parallel to the extent of reduction. The marked variation with rank of the effects of reaction suggest that here we have one suitable technique for investigating close distinctions among vitrinitic materials.

Hitherto in the study of the reduction of coals, attention has been chiefly concentrated on the variation of extent of reaction with rank, and little work has been done on the chemistry of the products. One interesting possibility is the

* The analyses quoted were made by United Analysts Ltd., East Boldon, Co. Durham, England, a laboratory experienced in coal analysis, and they are believed to be the most reliable data available. The samples have also been analysed in two other laboratories, with results that do not altogether agree with those quoted; however, these laboratories did not observe certain precautions now believed important (see Appendix), which were observed by United Analysts.

study of hydrogen distribution in the product by nuclear magnetic resonance spectroscopy. To get the maximum advantage from this technique, the material must be in solution, preferably in a solvent that contains no hydrogen. Deuteropyridine has been used for this purpose with solvent extracts of untreated vitrinites⁷ and reduced products.⁸ However, it is extremely expensive and the small proportion of isotopic impurities found in all commercial samples interferes with estimation of aromatic hydrogen in the solute. We have now found that 40-75% of that part of the reduction products of four vitrinites soluble in pyridine is also soluble in chloroform. A large number of solvents have been tested, most of which dissolved very little; piperidine, chloroform, dimethylformamide and dimethylsulfoxide dissolved significant quantities of product. Deuteriochloroform is relatively inexpensive, and since any isotopic impurity interferes little with the coal spectra, it is an excellent solvent for n.m.r. studies. So far we have only been able to run one spectrum in the solvent; the result is discussed later.

Four pure vitrinites have been reduced by the lithium-ethylamine technique. The amount of hydrogen added and the solubilities of the products in pyridine and chloroform are shown in Table 2. All the samples are of lower rank than that at which maximum reduction occurs; it will be seen that the pyridine solubilities are higher for the two samples of higher carbon content. Moreover the two samples MP 10a and 10b, taken from different levels in a single pillar section of a seam, behave differently; so also do the pair of vitrinites of the same reflectance but from different seams. The nitrogen contents of the products and the weak methyl absorption band at 1375 cm^{-1} in the infrared spectra show that the ethylamine is not retained by the products. Good oxygen balances were also obtained, showing that oxidation did not occur. Some pick-up of oxygen did occur, however, in some of the solvent extractions.

Table 2. Reduction of Vitrinites with Lithium

	Reduced Vitrinites			
	MP 10a	MP 10b	MP 11	MP 17
H atoms per 100 C atoms in product	115	87	107	91
H atoms added per 100 C atoms	37	11	31	15
Pyridine solubility, %	37	41	61	53
Chloroform solubility, %	27	18	45	16*

* Low solubility may in part be due to exposure to air.

The infrared spectra of the untreated vitrinite MP 11, the chloroform- and pyridine-soluble and -insoluble parts of the reduced products are shown in Fig. 2. It will be seen that all fractions of the product show increased aliphatic C-H absorption at about 2920 cm^{-1} and 1450 cm^{-1} (3.45μ and 6.9μ), the chloroform-soluble part showing the greatest increase. The extinction coefficients of the absorption at 2920 cm^{-1} calculated from the per cent transmission and the concentration in the potassium bromide discs (gm./gm.), are shown in Table 3, together with the H_{ar}/H_{al} ratios for the raw coals calculated from the absorptions at 3030 cm^{-1} and 2920 cm^{-1} , and an assumed $\epsilon_{ar}/\epsilon_{al} = 0.44$ (see refs. 9-11). The extinction coefficients for the products from different coal samples are approximately consistent with the extent of reduction derived analytically. The use of the extinction coefficient ratios must not be pushed too far as the value of the extinction coefficients is dependent not only on the concentration but also on structural factors.

In the spectra of all the reduced products, the absorption in the aromatic carbon-hydrogen bending region, $650-950\text{ cm}^{-1}$ ($11-15\mu$) was considerably weaker than

Table 3. Spectral Studies of Hydrogen Distribution

	Sample	Vitrinite			
		MP 10a	MP 10b	MP 11	MP 17
H_{ar}/H_{al}	Raw Coal	0.32	0.36	0.41	0.34
$\epsilon_{2920} \text{ cm}^{-1}$	Raw Coal	0.11	0.12	0.12	0.16
$\frac{\epsilon_{2920} \text{ (Product)}}{\epsilon_{2920} \text{ (Raw Coal)}}$	Crude Reduction Product	3.2	2.1	3.5	1.6
"	Pyridine Extract	3.6	1.5	3.6	1.3
"	Pyridine Insolubles	1.2	0.5	1.2	0.6
"	Chloroform Extract	3.6	2.7	3.5	2.2
"	Chloroform Insolubles	1.8	1.6	---	1.2

that in the untreated coals, and the C-H stretching vibration at 3030 cm^{-1} could not be distinguished at all in the spectra of any of the products but MP 17. A broad band centered at 1250 cm^{-1} and a broad shoulder and 1050 cm^{-1} were noticeable in the spectra of all the products. Similar but not identical spectra have been shown previously by Reggel *et al.*⁵ for the reduced products; these authors do not report spectra of solvent extracts of the products.

The n.m.r. spectrum of the chloroform-soluble part of the product of reduction of sample MP 10b is shown in Fig. 1. Owing to instrumental difficulties, it has not been possible to re-run this spectrum nor to run other samples or a solvent blank. However, the infrared spectrum of the solvent showed very high isotopic purity and little sign of the presence of hydrogen. The most striking feature of the spectrum is the extremely sharp doublet at chemical shifts of 2.87 and 2.95 p.p.m. (referred to tetramethylsilane). These peaks are in the position expected for hydrogen atoms on carbon in the α -position to an aromatic ring or double bond. Absorption in this region has been previously reported for certain coal derivatives, and so its presence here is not surprising. However the sharpness and the fact that the area under the peak is 50% of the total area under all peaks is surprising. As already noted, this result still awaits checking, but it is very difficult to imagine any possible impurity that could give a large sharp peak here but no similar sharp peaks elsewhere. Other peaks were observed corresponding to methyl and other aliphatic hydrogen (0.87, 1.25 and 1.45-2.0 p.p.m.) and aromatic and phenolic hydrogen (8.06 p.p.m.).

Dehydrogenation

It is already established that much of the aliphatic hydrogen in vitrinites and spore exinites is present in hydroaromatic rings.^{12,13} It has been argued that these rings play an important part in the structural make-up of these macerals¹⁴ and that they govern much of the maceral chemistry. The study of hydroaromatic structures by dehydrogenation is therefore important in any detailed study of macerals, but no fully satisfactory method has yet been reported. Peover¹² has described the use of benzoquinone as a dehydrogenating agent; it is efficient, but in a side-reaction, which Peover believed to be addition by a Diels-Alder reaction, a considerable proportion of quinone combines with the coal and cannot be removed. Peover mentions the use of triphenylmethyl perchlorate, but gives few details. Raymond *et al.*¹³ report catalytic dehydrogenation with palladium on calcium carbonate and other catalysts, in high boiling solvents such as phenanthridine. This method permits direct and accurate determination of the hydrogen removed, but it requires a rather high temperature (over 300°C) and there is apparently some difficulty in removing catalyst and solvent if the products are wanted for further study.

We have used 3,5,3',5'-tetramethyldiphenoquinone as a dehydrogenating agent for the Bruceton vitrain under the same conditions as Peover used for benzoquinone, thinking that this bulky molecule would not readily undergo Diels-Alder addition to the coal. The spectrum of the product showed little change from the untreated coal, except that a band at 1190 cm^{-1} (8.4μ) appeared. This band is in the region expected for either ether oxygen or carbonyl vibrations, and suggest some addition of the quinone to the coal; however, no carbonyl stretching absorption at $1660\text{-}1700\text{ cm}^{-1}$ was observed, in contradistinction to the situation when benzoquinone was used.

We have also used the free radical diphenylpicrylhydrazyl, $(\text{C}_6\text{H}_5)_2\cdot\text{NHN}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3$, which is reported to be an effective dehydrogenating agent for hydroaromatic rings.¹⁵ The infrared spectrum of the product indicated that some dehydrogenation probably occurred, but in most cases some addition of the hydrazyl to the coal took place. In one experiment a relatively small amount of the hydrazyl was used; it was found that in the ultra-violet spectrum of the filtered reagent solution after reaction the strong band at 3330 \AA characteristic of the hydrazyl had been completely replaced by a band at 3200 \AA characteristic of its reduction product, the hydrazine. We conclude that the reagent does dehydrogenate coal, but not very effectively.

It is believed that in dehydrogenation with the quinones, the hydrazyl and triphenylmethyl perchlorate, the first step in all cases is a transfer of hydride ion, H^- , from the hydroaromatic system to the reagent. This step would leave a carbonium ion, and the first stage of reaction must then be completed by loss of a proton, H^+ , so that the net result is elimination of a hydrogen molecule. Further hydrogen molecules are removed in the same way until the ring has become aromatic. Now some carbonium ions are known to be stable, and so it is possible that in the reaction of coals a proportion of the H^- loss is not followed by elimination of H^+ . The carbonium ions in the coal could then react with some species derived from the reagent, in an addition reaction. For example, if a quinone takes up H^- , the hydroquinone mono-anion is formed, and if this reacted with a carbonium ion, a covalently-bonded ether would result. If triphenylmethyl perchlorate is the reagent, then a coal carbonium perchlorate would result, in which the bonding is essentially ionic. We have, therefore, a possible explanation of why all four reagents add to the coal to some extent, which in the case of quinones would replace the Diels-Alder hypothesis. In the case of the perchlorate reaction, it should be possible on the above hypothesis to remove the perchlorate ion and a proton from the coal, thus completing the dehydrogenation step, by treatment of the product with a suitable base. We have investigated the use of triethylamine for this purpose.

Peover¹², and Cunningham, Given and Wyss (unpublished observations) found that the products of dehydrogenating some British vitrains with triphenylmethyl perchlorate weighed 30-50% more than the coal originally taken. J. K. Brown (unpublished) found absorption in the infrared spectra of the products characteristic of the perchlorate ion, but could find no sign of the presence of the triphenylmethyl group. We have dehydrogenated the Bruceton vitrain and the vitrinites MP 10a and 10b with the reagent, washed the product thoroughly with acetone, and find the weight increases shown in Table 4. The products were refluxed with triethylamine (b.p. 89.5°C) and suffered the losses in weight shown in the Table. It will be seen that with the two vitrinites the addition of reagent was relatively small, but nearly the whole of it was apparently eliminated by amine treatment.

In the infrared spectra of all the dehydrogenated products, the aliphatic C-H bands at 2920 and 1420 cm^{-1} (3.45 and 6.90μ) were decreased in intensity. All the spectra showed a broad region of absorption between 1030 and 1120 cm^{-1} (8.9 to 9.7μ), that is, in the position where the perchlorate ion absorbs strongly. This absorption was completely removed by the amine treatment. The products also showed well-defined absorption in the aromatic C-H bending region at 698 and 745 cm^{-1} , which was not removed by amine treatment. The triphenylmethyl group in the perchlorate and the alcohol absorbs strongly at 698 and $753\text{-}760\text{ cm}^{-1}$; in spite of the fact that the second frequency is somewhat higher than that in the spectrum of the coal products, this suggests

that some triphenylmethyl anion or triphenyl methane is retained by the coal. On the other hand, dehydrogenation will increase the aromaticity of the coal, and this should cause increased absorption in this general region.

Table 4. Weight Changes in Dehydrogenations with Triphenylmethyl Perchlorate

	<u>Bruce-ton vitrain</u>	<u>Vitrinite 10a</u>	<u>Vitrinite 10b</u>
Wt. gain in reaction, %	36	16	18
Wt. loss on amine treatment, % of wt. of untreated coal	12	14	17

There were indications in the spectra that vitrinite MP 10b was somewhat more extensively dehydrogenated than 10a.

There is therefore some support for the suggestion that the perchlorate ion at least is retained in the coal products on carbonium ions which are intermediate products of the dehydrogenation, though perhaps it should not yet be regarded as proved. Amine treatment is fairly effective in removing the ion. The matter is under further investigation.

As an alternative approach to the study of dehydrogenation, we are using C¹⁴-labelled benzoquinone, in the hope that a radiochemical determination of quinone retained will permit us to correct elementary analyses of the products to a quinone-free basis. The method will also facilitate study of the removal of the quinone.

General Discussion and Conclusions

We believe that the introduction of chloroform as a solvent for vitrinites reduced with lithium in an amine represents a significant advance, which should facilitate further study of the chemistry of the reaction and the application of n.m.r. techniques. It should prove particularly useful with vitrinites of higher rank than those used here, where higher solubility is to be expected, and on the present evidence the study of the reaction and its products does provide a sensitive means of distinguishing between closely related macerals. The single n.m.r. spectrum of a reduced product so far obtained suggests a number of detailed interpretations with most interesting implication for coal structure, but these will not be discussed until more data are available.

Some contribution to the understanding of the mechanism of dehydrogenation reactions has been made, but it cannot be claimed that a fully satisfactory procedure has yet been found. Information merely about the amount of hydrogen removable, without any further study of the products, would be useful in the study of macerals, and of the methods available at present for obtaining it, the catalytic method¹³ is perhaps the best.

There is now available a fairly detailed set of data on two pairs of highly purified vitrinitic materials. It has been established that between the members of each pair there are significant differences in elementary composition, in distribution of hydrogen and of oxygen functional groups, and in response to lithium reduction. In the case of the pairs from the same pillar section, the chemical differences are matched by a difference in reflectance. The reflectances of the two coals of different geological age do not differ much, but we must conclude that in spite of this the samples are of somewhat different rank in a chemical sense. This apparent discrepancy between petrographic and chemical rank may be associated with the difference in age and origin.

The results throw some light on the problem of the heterogeneity of the vitrinite group of macerals, but more data are obviously required before firm conclusions can be stated.

Experimental

Spectra. All infra-red spectra were run in a Perkin-Elmer Model 21 Spectrophotometer; the samples were dispersed in KBr pellets, a blank KBr window being placed in the reference beam. In order to obtain reliable optical densities, the weight of samples was taken to the nearest 0.01 mg. on a micro-balance, and the window thickness was measured with a micrometer. Peak heights were measured by the base-line technique.

The n.m.r. spectrum was run on an approximately 2% solution of material in deuteriochloroform. A Varian A-60 spectrometer was used.

Lithium Reductions. The procedure previously described⁴ was followed; approximately 1 gm. coal samples were taken in each experiment, and 8 hrs. reaction time was allowed. The extractions of the products were run on 0.1 - 0.2 gm. samples, which were shaken mechanically with 4-6 ml. solvent at room temperature for 24 hours. To recover the extracts, solutions were evaporated slowly under nitrogen and the residues dried in vacuum at 100°.

Dehydrogenations. 3,5,3',5'-Tetramethyldiphenquinone was prepared by the oxidation of 2,6-xynolol with benzoyl peroxide in chloroform.¹⁶ In the dehydrogenation reactions, 0.3 gm. coal was refluxed with 1.2 gm. of the quinone in 30 ml. dimethylformamide under nitrogen for 5-1/2 hours.

In the use of diphenylpicryl hydrazyl, 0.1 gm. coal was refluxed with 0.3 gm. hydrazyl in 30 ml. of either pyridine or chloroform for various lengths of time up to 24 hours.

The above methods were applied only to the Bruceton vitrain.

The reactions with triphenylmethyl perchlorate were run as follows. About 1 gm. coal was refluxed with 10 gms. perchlorate in 50 ml. glacial acetic acid for 30-35 minutes. After cooling the liquid was poured into acetone (to dissolve the triphenylmethane formed and any unchanged perchlorate) and filtered. The residue on the filter was shaken mechanically in a further 100 ml. acetone for 5-8 hours, filtered, washed on the filter with more acetone, and dried. A portion of the product (about 0.2 gm.) was refluxed with triethylamine for 2 hours; the liquid was cooled, and filtered, and the product was washed thoroughly with methanol and dried.

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Appendix: Elementary Analysis of Coal Samples

As a result of experience accumulated during the research reported here, we have reached certain conclusions about the preparation of samples for analysis and about analytical procedure, which we wish to place on record.

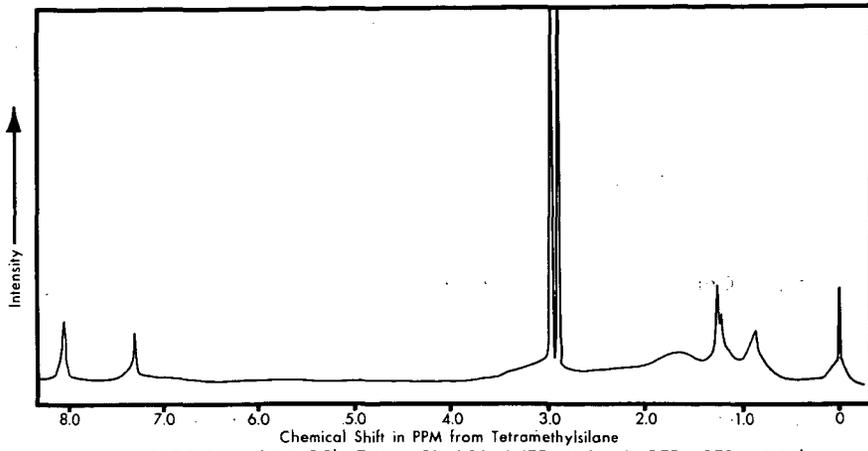
1. Samples should be submitted for analysis and analysed in an undried condition. The moisture content should be determined carefully at the same time as the other determinations, and the hydrogen and oxygen contents corrected appropriately.

In conditions of medium to high humidity and relatively low temperature, well dried coals are very hygroscopic and can absorb moisture from the air while being handled and weighed.

2. Freshly mined samples and samples that have been separated by float-and-sink in organic solvents should be thoroughly dried, and then allowed to come to equilibrium with moist nitrogen at a suitably controlled humidity. This prevents methane, solvents, etc. being determined as moisture. The controlled humidity can be chosen so that any change of weight on exposure to moist air is slow.

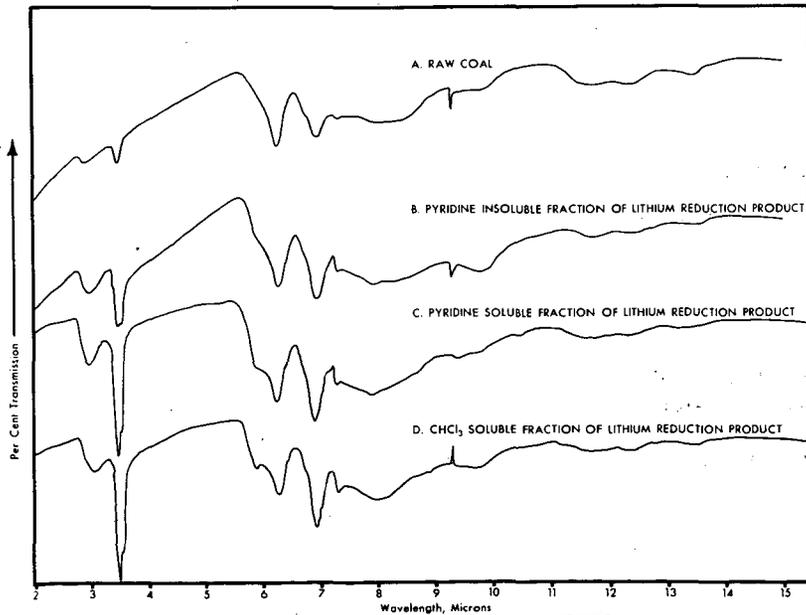
3. Ash should be determined separately, as in a proximate analysis; weighing the residue after the combustion for the C and H determination is not reliable.

4. Wherever possible, oxygen should be determined directly; by comparing the sum of the various determinations with 100% a valuable check on the correctness of the whole analysis is obtained.



NMR SPECTRUM OF DCCl_3 EXTRACT OBTAINED FROM Li REDUCED MP-10b

Figure 1



IR SPECTRA OF VITRINOID MP-11 AND ITS REDUCTION PRODUCTS

Figure 2