

The Use of Radioactive Tracers in Studying Functional Groups in Coals

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In the classical organic chemical method of elucidating the structure of an unknown substance reactions are carried out with reagents that would be expected to react only with one kind of functional group or in some other specified way. The product is purified from excess reagent and by-products, for example by crystallization to constant melting point; it is then analysed and characterized by further specific reactions. Thus if the original substance were a secondary alcohol, it might be oxidized selectively to a ketone, and the character of this established, after purification, by conversion to a phenylhydrazone.

In the chemical study of coal it is not easy to find selective reagents. Different functional groupings in coal often have similar reactivities. Moreover, a single type of group may exhibit a spread of reactivity owing to its occurrence in the coal in a variety of environments; consequently attempts to achieve completeness of reaction usually incur a loss of selectivity. The only purification of reaction products possible, since coal is an involatile solid and only partly soluble, is washing with some suitable liquid to remove excess reagent. Inadequate purification often causes serious difficulties, since in many reactions it has proved impossible to remove adsorbed or otherwise strongly held reagent (for example, chloromethylation catalysed by stannic chloride¹, dehydrogenation with benzoquinone² and triphenylmethyl perchlorate³, reduction with lithium and aliphatic amines⁴). Consequently characterization of the product by elementary analysis is made difficult or impossible; other properties, such as the infra-red spectrum may also be affected.

It is the purpose of this paper to develop and illustrate the thesis that some at least of the difficulties outlined above can be obviated by the judicious use of reagents labelled with radioactive atoms. Neutron activation analysis, in which tracer atoms are generated *in situ* by suitable irradiation, might be useful in coal research, for example in determining the silicon content of trimethylsilyl ethers⁵; however this type of analysis is a special case and will not be discussed further (in any case it has not yet been applied to coal so far as the author is aware).

It is difficult to classify in any rational manner possible applications of tracer techniques to organic chemical studies of coal. Therefore three researches in which tracers were used will first be described briefly and the advantages of the technique in these cases will be analysed. Subsequently attention will be drawn to a number of other reactions where the technique would be valuable. It is hoped thus to show inductively the range of application.

1. Carbonyl and Hydroxyl Groups

The interpretation of the band at 1600 cm^{-1} in the infra-red spectra of coals as due in part to the presence of carbonyl groups⁵ has been sharply contested⁶. But if it can be shown on other evidence that these groups are present, then the spectra indicate that they must be strongly conjugated and probably chelated to hydroxyl. Carbonyl groups of this type either do not react or react abnormally with the usual reagents⁷; attempts to determine carbonyl in coal with hydroxylamine⁸ and

*The author is indebted to Dr. P. S. Skell for this suggestion.

phenylhydrazine⁹ proved unsatisfactory. Treatment with lithium aluminum hydride produced no detectable change, probably because the hydroxy groups formed were re-oxidized very readily during working up of the product.

Given and Peover¹⁰ therefore used radioactive tracer technique with coal extracts in what was essentially a reductive acetylation reaction, the reduction being carried out by electrolysis in dimethylformamide solution. Quinones reduced in this way yield the dianions of the hydroquinones, which react rapidly at room temperature with acetic anhydride to give the hydroquinone diacetates and acetate ions. An extract acetylated with unlabelled reagent was reduced at a stirred mercury cathode controlled at a series of standard potentials against a reference electrode; in this way the reducing power of the system could be varied at will. The quantity of electricity passed was measured with a coulometer. When the current had fallen nearly to zero ¹⁴C-labelled acetic anhydride was added. The product was isolated, washed with unlabelled acetic acid and water to remove adsorbed radioactive acid, and the disintegration rate counted. Counting was continued until about 10,000 had been recorded. The count rate was 2000-8000 min.⁻¹.

When acetylated but unreduced materials were treated in DMF with labelled anhydride the count rate of the product was about 90 min.⁻¹. Hence neither adsorption of ¹⁴C-acetic acid nor ester exchange with ¹²C-acetyl was significant. A further confirmation of this was obtained by determining first the hydroxyl content radiochemically, with the result: O as OH = 4.9%. The radioactive product was then reductively acetylated, again with labelled anhydride. The final count rate gave: total O as OH + CO = 9.3%; hence, by difference, O as CO = 4.4%. The latter value is to be compared with the value 4.0% obtained by direct radiochemical determination as described above on a separate sample of the same extract. Over 90-95% of the radioactivity of the various products was removed by hydrolysis with sulfuric acid, showing that no significant C-acetylation occurred.

Thus the use of tracer technique provided:

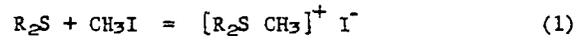
1. unequivocal proof that fresh hydroxyl groups are produced by reduction, that is, that carbonyl groups are present
2. an easy means of checking the absence of a possible side-reaction
3. a simple routine method of studying the variation of carbonyl content with fraction of coal extracted and rank of coal
4. simple means of following the distribution of carbonyl groups as a function of their reduction potentials
5. a check on the selectivity of the reduction.

Points 4 and 5 merit some further comment. A "carbonyl content" could be calculated not only from the ¹⁴C-acetyl content but also from the number of coulombs consumed; both were plotted against the controlled potential (see example in Fig. 1). The coulometric figure was somewhat higher than the radiochemical at potentials up to about -1 volt (measured against mercury pool in 0.1N tetraethylammonium iodide as reference electrode). Moreover whereas the radiochemical figure levelled off to an approximately constant value at potentials in the range -1 to -1.4 volt (varying with the coal), the coulometric increased without limit. Hence other groups than carbonyl were reduced, particularly at higher potentials; these were presumably aromatic nuclei. Also shown in Fig. 1 is an approximate distribution curve for radiochemical carbonyl content as a function of reduction potential, from which some deductions about the nature of the carbonyl groups can be made (see ref. 10 for details). In conclusion, it must be admitted that comparison of the infra-red spectra of the coal extracts and their acetylated and reductively acetylated products introduced some uncertainty in the interpretation of the data for carbonyl contents. Depending on the view one takes of the significance of the spectra, the carbonyl contents of extracts of bituminous vitrains of carbon content 78-89% are either in the range 2.2-0.9 or 4.4-1.8% O as CO (decreasing with increasing rank). In either case 65-90% of the oxygen was accounted for as OH + CO.

Since this work was done, it has been shown¹¹ that finely ground whole coals can be reduced in suspension in DMF. It would therefore be worth applying the radiochemical technique for carbonyl determination to coals; this has not yet been tried. If the conventional reductive acetylation technique (refluxing with zinc, acetic acid, etc.) were applied to acetylated coal using labelled reagents, ester exchange would certainly occur and invalidate the results; however it would be possible to use labelled reagents for both steps, and determine carbonyl by difference.

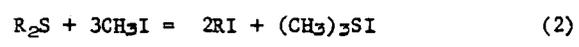
2. Sulfur in Coals

It is commonly supposed that the organic sulfur in coals is present in any or all of the forms, mercaptan, disulfide, sulfide, thiophene ring system; the last two, on grounds of superior stability, are the most probable¹². Of these four forms the first three react (at varying rates) with methyl iodide to form tertiary sulfonium iodides¹². The primary reaction with a sulfide is:



With mercaptans and disulfides hydrogen iodide and possibly other by-products are also formed.

Selker¹³, in a study of sulfur in vulcanized rubber, showed that further reaction can occur, involving a metathesis of the radicals attached to sulfur, by dissociation and re-methylation; the rate of reaction varied widely with the nature of R. The overall result is:



Thus, when applied to coal, by reaction (1) one methyl group and one iodide ion are introduced for each sulfur atom present as sulfide, whereas by reaction (2) two covalently bound iodine atoms are added to the coal and one molecule of trimethylsulfonium iodide released into solution for each sulfur atom present; in the latter case the sulfur is removed from the coal.

Reaction with methyl iodide has been used by various authors¹⁴⁻¹⁶ to obtain a distribution between the reactive and unreactive forms of sulfur. Kavcic¹⁴ and Angelova¹⁵ assumed that only reaction (2) took place, and measured the decrease in sulfur content. Postovskii and Harlampovitch¹⁶ assumed only reaction (1) and measured the iodine content of the treated coal.

Experiments have been started¹⁷ with the object of finding out which reaction is in fact followed, using ¹⁴C-labelled methyl iodide. The coal is heated at 125° with the iodide in acetone. The product after washing with acetone is analysed for ¹⁴C, and for total S and I by chemical analysis; a sample is washed with sodium nitrate solution and the iodide ion released by exchange is determined by titration. The results still require some clarification, but it is already evident that both reactions (1) and (2) occur, since some sulfur is removed, and both covalent iodine and ¹⁴C-methyl groups are added; there is some exchangeable iodide ion in the products.

A complex reaction like this can obviously only be elucidated by setting up a complete weight balance for methyl, bound and ionized iodine, and sulfur. Radiochemical methods cannot be used for the sulfur, and are hardly necessary for the iodine, since its atomic weight is high and chemical analysis is reasonably accurate (though perhaps slower than radiochemical). However the carbon and hydrogen added as methyl could not feasibly be determined in any other way than by means of tagged atoms.

Perhaps it is worth mentioning for completeness that Ceric has carbonized a series of coals in the presence of added ³⁵S-enriched pyrite¹⁸; she found that some of the sulfur released by the pyrite becomes fixed in the organic part of the char. She also used the same tracers in studying the effect of carbonizing in a stream of

hydrogen, steam and ammonia.

3. Depolymerization of Coal

The depolymerization of coal with the phenol/boron trifluoride complex studied by Herydy and Newworth¹⁹, illustrates another use of tracers. In this reaction, the Lewis acid brings about the splitting of linkages of the diarylmethane type, and one molecule of phenol adds across each broken bond. The coal is broken down into products of relatively low molecular weight, a large fraction being soluble in organic solvents. The use of ¹⁴C-labelled phenol permits the amount added to the fragments to be easily determined. The results, in conjunction with the molecular weights of fractions and other data, suggest interesting conclusions about coal structure and in particular the way in which aromatic nuclei are linked together.

4. Suggested further Applications

(a) Performic acid oxidation. Early experiments¹ showed that the extent of oxidation of a coal, measured by elementary analysis and by the solubility of the product in caustic soda, was much reduced if the coal was first acetylated. This result, if correct, is important, because it implies that the initial attack of the reagent is on the aromatic nuclei, rather than aliphatic groupings, as might have been expected. However later experiments^{20,21} did not confirm the result, and it was suspected that since they were on a larger scale and a higher temperature was reached owing to the strongly exothermic nature of the reaction, the acetyl groups were removed by hydrolysis in the strongly acid reagent. The use of ¹⁴C-acetylated coal would provide the easiest means of testing this hypothesis.

(b) Dehydrogenation of Coals. Peover² found that the main reaction between coal macerals and benzoquinone was hydrogen abstraction from hydroaromatic rings and reduction of the quinone to hydroquinone. However, some Diels-Alder addition of quinone to the coal occurred, and consequently the analytical data were difficult to interpret. Interpretation would be easier if the quinone were labelled with ¹⁴C, or perhaps tritium.

(c) Other reactions. There are many other reactions where tracer techniques would greatly assist interpretation of the results, such as oxidation with perbenzoic anhydride¹, reduction with lithium in ethylene diamine⁴, and bromination with N.bromosuccinimide.

Conclusions

It is evident from the foregoing that tracer techniques are extremely useful in elucidating the reactions of coal, which are often complex. In particular the techniques offer the best and sometimes the only practicable means of finding out whether a reagent has added to the coal; this addition may be desired or undesired. In any event quantitative data are readily obtainable.

Where the facilities of a radiochemical laboratory are already available, the technique should clearly be used extensively. Provided a counting chamber of the hemispherical or cylindrical types is available, the radioactive reagent can be very heavily diluted with inactive material while still retaining an adequate count rate in the reaction product. Given and Peover in their reductive acetylation experiments¹⁰ only had available an end-window type of counter, so that 1 mc. of ¹⁴C-acetic anhydride could be diluted only to about 20 ml. Where one of the high-efficiency counting chambers is available, 1 mc. could be diluted to many litres; at this dilution 20 ml. reagent used in an acetylation would cost considerably less than a chemical acetyl determination carried out by a commercial microanalytical laboratory. Radiochemical methods therefore may prove not only convenient and useful, but perfectly practicable for extensive use.

References

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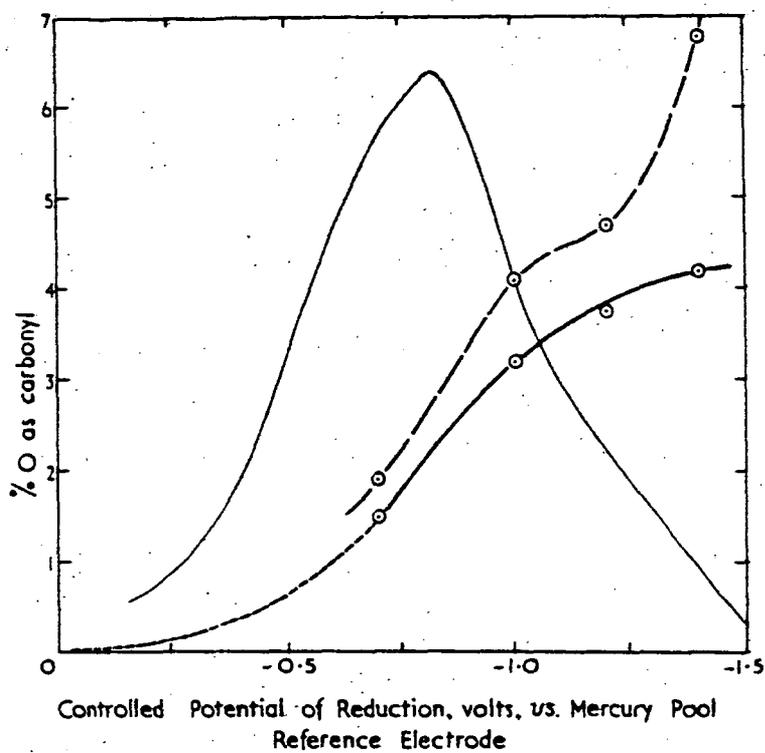


FIG. 2. Variation of apparent carbonyl contents of pyridine extract of coal DIII with potential.

- Radiochemical figures.
- - - Coulometric data, assuming all carbonyl quinonoid.
- Approximate distribution curve of carbonyl content with potential.