Carbonyl Groups in Bituminous Coals

IN a recent communication¹, the use of trimethyl-acetoaminohydrazide hydrochloride (Girard's reagent-*T*), for determining the carbonyl content of vitrains in bituminous coals, was reported. For reasons discussed here, the application of this method to coals is open to serious objections.

Girard's reagent-*T* is a specific reagent for ketonic carbonyl groups and has been widely used for the extraction of carbonyl compounds from mixtures of, for example, steroids. Its successful operation depends on separation of the carbonyl compound from the inert material by formation of a water-soluble derivative. Thus the application of this reagent to coals involves the assumption, in the first place, that carbonyl-containing molecules in coals will react to form water-soluble materials and that no carbonyl groups remain in the insoluble residue. In presenting their results, the authors have made the further implicit assumption that coals are mixtures of different types of molecules, some of which contain carbonyl groups and others which do not.

A considerable amount of work has, in recent years, been devoted to the study of coal constitution. One of the more important results of this work has been to show that the vitrainous component of a coal consists, for the main part, of a large number of chemical units which differ considerably in size but are closely similar in type²⁻⁴. In addition, vitrains are generally associated with small quantities of materials (for example, resins) which are structurally different from the bulk of the coal and cannot be regarded as characteristic of the coal substance⁴. In other words, the various functional groups in coals (for example, OH, C=O) are distributed among all the molecules comprising the coal structure, in much the same way as they would be in an unfractionated polymer, and are not concentrated in any particular fraction. This very general picture makes clear why it has not proved possible, in the past, to separate different molecular species from coals by the usual methods of fractionation⁵. Such molecular-weight measurements as have been made indicate that the average molecular weights of solvent extracts of coals range from about 1,000 to 4,000 (refs. 6 and 7), and it is a fair assumption that the insoluble residues contain molecules of considerably higher molecular weight.

It is thus very improbable that any but the smallest molecules in coals would be rendered water-soluble by condensation with Girard's reagent. So far, therefore, from representing maximum values of carbonyl content of coals, as claimed by the authors, the figures obtained by the use of Girard's reagent probably refer either only to a very small, low-molecular-weight coal fraction or to unrepresentative resinous materials or even to oxidative degradation products produced during the reaction itself. It appears, further, that the calculation of "maximum values" of C=O from the weights of the 2:4-dinitrophenylhydrazones is based on the assumption that the carbonyl compounds are present as pure carbon monoxide. The authors' "maximum values" are thus too high by a factor of 2-3 compared with "realistic values". It should be borne in mind that, even so, the "maximum values" of carbonyl found by the authors represent, with one exception, only about 1 per cent of the total oxygen content of the coals; for a similar range of coals, previous authors^{8,9}, using other methods, have found carbonyl contents corresponding to 5-25 per cent of the total oxygen.

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It has been conclusively demonstrated previously that Girard's reagent is capable of condensing with high-molecular-weight ketonic substances in the presence of large masses of inert material to form hydrazone derivatives having a polar group which renders them soluble in water¹. Thus it is not unreasonable to expect (not "assume") that ketonic substances even in a material as complex as coal will undergo the condensation reaction with Girard's reagent provided steric hindrance effects are not too great.

At this point it is necessary to digress in order to clarify a point on coal constitution, since we feel that Mr. Wyss's objections stem largely from the fact that his views on this matter differ materially from our own. It is generally agreed that coal consists either of a molecular aggregate comprising molecules of different structures and sizes or of chemical units which are large in size but closely similar in type. Recent work in this Department² has shown that different molecular species can be separated from coals by chromatographic fractionation of their pyridine extracts on alumina columns followed by identification of the fractions using infra-red spectroscopy. Molecular-weight determinations using a sensitive thermo-electric osmometer show that it is possible to separate materials with number-average molecular weights as low as 250. Molecules of this size have also been found in the acetone fractions of humic acids³. Although not conclusive, this evidence lends some support to the former view on the chemical constitution of coal. Admittedly these values refer to solvent extracts; but it is very likely—though not absolutely certain—that such molecules were present in the original coal: the action of the solvent probably causing dispersion of the molecular aggregates to yield quantities of truly dissolved material rather than scission of chemical bonds to generate molecules smaller than the original.

The question now arises: What is the upper limit of size of organic molecules on which a polar group confers solubility in water? The only evidence we can offer in this respect is afforded from the results obtained using an extension of our technique in which the carbonyl contents of the pyridine extracts of the same series of vitrains were determined⁴. Volumetric determination⁵ of the excess of 2,4-dinitrophenylhydrazine (10 gm./l.) using a standard solution of titanous chloride has enabled the weight-average molecular weights of the ketones involved to be estimated. The values range from 171 at 82 per cent