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A Novel Method for Controlled Oxidation*

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The purpose of this paper is to describe a novel method for the oxidative degradation of coal or other organic material. The procedure is potentially useful for structure determination. As originally conceived, this method was intended for use with aqueous potassium permanganate as oxidant, but it is equally applicable with other oxidizing agents. Sodium hypochlorite can be substituted for $KMnO_4$ except that controlling the pH and monitoring the end point become more difficult. Results with potassium permanganate only will be described here but sodium hypochlorite was tried. An advantageous feature of the method is the simultaneous removal of soluble products from further contact with oxidizing agent as the oxidizing agent attacks the substrate. In principle, the experimental approach resembles that of column chromatography.

Any oxidative degradation of a natural product for structure determination is of little use if carried out too far; for example, to the smallest, most oxidation-resistant materials such as carbon dioxide, acetic acid, and benzoic acid. Potassium permanganate oxidations of reactive species such as coal and kerogen are particularly difficult to control. Partially oxidized fragments which go into solution can be attacked more effectively than the solid starting phase, a situation which results in loss of structural information. Bone and coworkers,[2] as well as Djuricic,[3] in their classic works, attempted to preserve labile products by conducting stepwise partial oxidations. These procedures are cumbersome and involve numerous manipulations to remove unreacted starting material and manganese dioxide. Another difficulty is that phenolic materials[4,5,6] can undergo coupling reactions thus generating larger molecules and giving misleading results due to a larger number of substituents.

The procedure is quite simple. An example is described for the degradation of coal. Illinois #6 vitrain (100 g ground to < 250 uM) was mixed with 100 g of Celite #503, and the mixture was ground further in a ball mill. The resulting powder was then mixed with 800 g of Celite. This mixture was poured into a glass column 5 cm by 130 cm which contained a pad of sand and a pad of Celite 6 cm thick on a coarse scintered-glass support. A 600-ml reservoir on top of the column was filled with a saturated aqueous solution of potassium permanganate. About 10 days was required to percolate the solution (790 g of $KMnO_4$ in 15 l of water) through the column. Although the reaction requires little attention, the time could be reduced considerably by reducing the pressure at the receiver. The course of the reaction could be followed by the heat detected in a 5-cm band as the reaction progressed down the column. The reaction was terminated when permanganate color appeared in the Celite pad at the bottom of the column. The oxidation was nearly complete; the coal left on the column weighed only 4 g and could be made to react with only 5 g of $KMnO_4$. Recovery of the unreacted material gave about 1 g of a black solid that resembled amorphous carbon and that contained 0.4 g of HF-soluble siliceous material. The alkaline effluent from the column was extracted with ether; the extract contained a negligible amount (~ 0.05 g) of neutral material. The volume of alkaline solution was reduced to 500 ml by means of a rotary evaporator, chilled on ice, and acidified with cold 6 $\underline{N}$ aqueous HCl. The accompanying

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evolution of CO_2 stopped after the addition of 2.0 to 2.1 moles of HCl. The carboxylic acids were removed by continuous ether extraction for 150 hr to afford 52.7 g of carboxylic acids. After ether extraction the aqueous phase that remained was heated at 40°C./50 Pa to remove the water. The residual dried and crushed salts were extracted by percolating boiling tetrahydrofuran through them for 24 h. Vacuum distillation of the tetrahydrofuran left 24 g of a tacky almost-black material that readily absorbed moisture from the air and had a caramel-like odor. A small sample of that material was exchanged once with D_2O, pumped dry, and again dissolved in D_2O for n.m.r. measurements on a 100-MHz instrument. The n.m.r. spectrum showed five broad peaks between 1.4 and 5 ppm. The chemical shifts were measured with respect to Me_4Si (external). The spectrum consisted of a small peak at 1.4 ppm, large peaks at 1.85 and 3.68 ppm, and intermediate sized peaks at 4.35 and 4.95 ppm. The material, which contained hydroxylated aliphatic acids, was not investigated further.

One aliquot of the ether-extracted acids was partially distilled. Another aliquot was converted to the ^{14}C-methyl esters for analysis on a gas chromatograph equipped with a radioactivity monitor. Normal aliphatic acids through butyric acid were isolated along with the dibasic oxalic, succinic, 2-methyl succinic, and glutaric acids. The n.m.r. spectrum indicated the presence of malonic and pimelic acids, but those acids could not be isolated in amounts sufficient for identification by other means. The aromatic acids: benzoic; o-, m-, and p-phthalic; 3-methyl phthalic; 4-methyl phthalic; hemimellitic; and trimellitic were found. Formic, acetic, oxalic, succinic, and trimellitic acids were most abundant. Van Krevelen[7] considered it significant that benzoic acid had not been found in a single case where conventional oxidation procedures were used, but we showed by isotope dilution that a small amount of benzoic acid was formed in the single stage oxidation of Illinois #6 vitrinite using potassium permanganate. In this study, attempts to isolate mellitic acid (benzenehexacarboxylic acid) by the method of Bone et al.[2] were unsuccessful. The yield of CO_2 in the percolation procedure is much less than the approximately 40% reported by Bone et al.[2]

Efforts to economize on the use of Celite were disastrous — the pressure produced by in situ generated manganese dioxide invariably burst the tubes. No difficulty was experienced when at least 8 to 10 parts (w/w) of Celite was mixed with 1 part of the ground coal. Flow rates were also improved by the higher Celite-to-coal ratios.

Not all coals are adaptable to this procedure; North Dakota lignite (PSOC-246) is usually oxidized through the first 15 cm of the column, and then the flow stops. The plugging of the column might be caused by the formation of $Al(OH)_3$ or by chemical comminution of the coal which may produce the layer of black substance that forms on the sintered-glass support. Materials that are soluble in a non-reactive solvent are easily dispersed in Celite by tumbling them together with the solvent and Celite in a rotary evaporator and them removing the solvent under vacuum. This method of dispersal was used in the oxidation procedure described[8] for 4-methyl-2,6-di-tert-butylphenol, a compound found[9] to be loosely bound to Yallourn brown coal. It is interesting to compare the results of a batch oxidation of the above hindered phenol with the results of the controlled column (or percolation) oxidation. A brief account is given here and further details can be found in Ref. 8. Batch oxidation of 4-methyl-2,6-di-tert-butylphenol gave principally the two dimers, 4,4'-ethylene-bis[2,6-di-tert-butylphenol] (1) and 2,2', 6,6'-tetra-tert-butyl-1,1'-stilbenequinone (2) and a smaller amount of another dimer 2,6-di-tert-butyl-4-(3',5'-di-tert-butyl-4'-hydroxybenzyl)-4-methyl-2,5-cyclohexadiene-1-one (3), Figure 1. Although small amounts of other compounds were isolated, it is obvious that further oxidation would give derivatives of 1, 2, and 3, reflecting their structure rather than that of the starting material.

The controlled oxidation of 4-methyl-2,6-di-tert-butylphenol did not give dimers in the column effluent. A small yield of a mixture of neutral compounds was isolated. These compounds, 4, 5, 6, 7, 8, 9, 10 are described in Fig. 2. The acid fraction contained formic acid, acetic acid, and pivalic acid and a mixture of hydroxy and keto acids which could not be separated.

Compound 4 contains a CH_2 group. It probably is derived from the aromatic ring accompanied by hydrogen migration. Compounds 5, 6, and 7 are the result of ring contraction while 8, 9, and 10 are more like the original material.

Although the latter results demonstrate the complex nature of interpreting oxidation results in terms of structure, we believe the method presented has valuable potential. The scope of the method should be extensively investigated with other oxidizing agents and model compounds, and we offer our initial results for a start in that direction.

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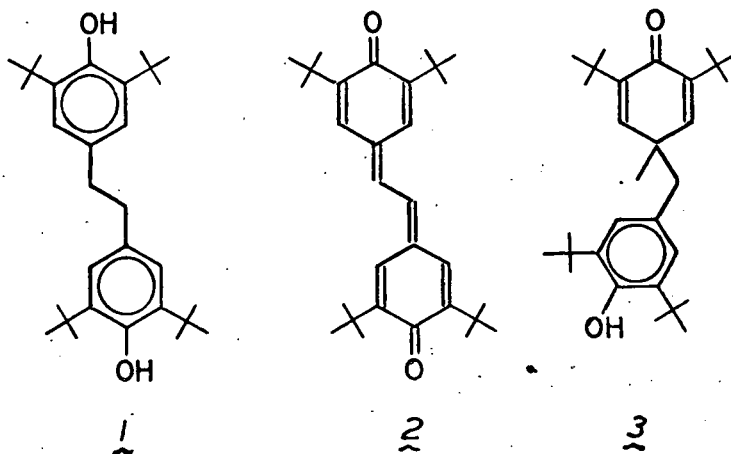9. Swann, P. D., Harris, J. A., Siemon, S. R. and Evans, D. G. Fuel 1972, 52, 154.

Figure 1. Products of batch oxidation of 4-methyl-2,6-di-tert-butylphenol with potassium permanganate.
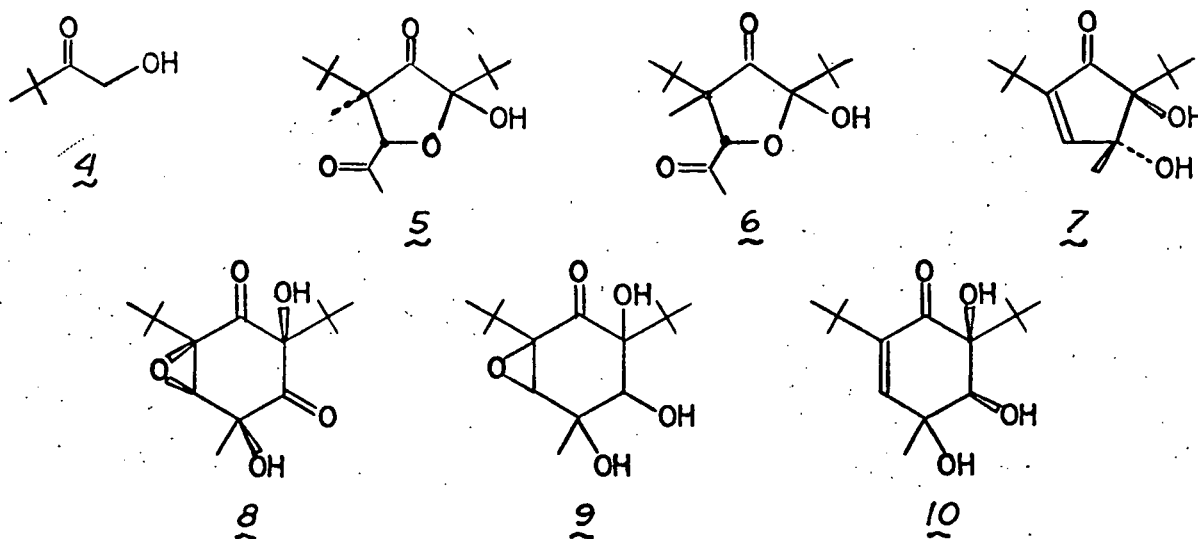

Figure 2. Products of column oxidation of 4-methyl-2,6-di-tert-butylphenol with potassium Permanganate