HPLC AND PHASE TRANSFER CATALYSIS IN THE ANALYSIS OF OXIDATION PRODUCTS OF LIGNITE LIQUIDS AND MODEL COMPOUNDS

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The objective of these studies was to develop new methods for the analysis of the types and quantities of aryl groups and alkyl groups present in the alkylarenes and hydroarenes which are major constituents of the liquefaction products derived from lignite coals. A number of oxidation reactions of light oil hydrocarbon mixtures and model compounds were investigated. In order to get high yield oxidation reactions, phase transfer catalysts were utilized in some of the reactions. Derivatization of the reaction products to give highly UV absorbing compounds facilitated the analysis of the products with HPLC.

Trifluoroperacetic acid has been described as a useful reagent for the analysis of alkyl groups since it easily degrades the aromatic rings present in the structure and gives aliphatic carboxylic acids incorporating the alkyl groups(1). Unfortunately, mixtures of products have been obtained from the oxidation of single compounds;(1,2) e.g., indan gave 27% succinic and 27% glutaric acids(1). Surprisingly, tetralin was reported to yield cyclohexene-1, 2-dicarboxylic anhydride as the only product (1).

Tetralin was oxidized at 60° using Deno's procedure(1) and the resulting acid mixture was converted to the p-bromophenacyl esters by refluxing with

p-bromophenacyl bromide in 50% ethanol-water at pH=6.8. The esters were analyzed on a 10μ Spherisorb-ODS HPLC column using a programmed gradient elution of methanol-water (Figure 1C). The program was devised so that the monoesters can be eluted followed by the diesters (see Table 1). The major components of the product mixture were succinic, glutaric and adipic monoesters and diesters (Figure 1A). The peaks corresponding to the p-bromophenacyl monoester of cyclohexene-1,2-dicarboxylic acid and the ethyl p-bromophenacyl mixed ester were very small. Since a unique product was not obtained from tetralin nor from most other hydroaromatics and alkylarenes, it is difficult to see how any quantitative information about coal or coal oil structure can be obtained with this method of oxidation.

TABLE 1

Peak No.	Retention Time, (min.)	Compound
1	4.0	succinic mono ester
2	5.5	glutaric mono ester
3	7.4	adipic mono ester
4	15.9	p-bromophenacyl alcohol
5	20.3	p-bromophenacyl trifluoroacetate
6	21.5	p-bromophenacyl bromide
7	28.5	succinic diester
8	29.8	glutaric diester
9	30.1	adipic diester
10	17.2	mono p-bromophenacyl cyclohexene-1,2-dicarboxylate
11	28.8	p-bromophenacyl ethyl cyclohexene-1,2-dicarboxylate
12	34.5	di p-bromophenacyl cyclohexene-1,2-dicarboxylate

Oxidation of a light oil from the liquefaction of Beulah, N.D. lignite with synthesis gas at 460° and 27.5 MPa (3) was carried out with CF_3CO_3H-H_2SO_4. HPLC analysis (Figure 2) of the p-bromophenacyl esters of the reaction products exhibited peaks corresponding to a range carboxylic acids in the range of 4 to 9 carbon atoms.

The oxidation of aromatic rings with RuO_4 was investigated as an alternative to the trifluoroperacetic acid method. Since yields reported in the literature (4) vary

considerably for this reagent, the use of a phase transfer catalyst to bring the oxidizing agent for RuO_2 into the organic phase was studied. The reaction of tetralin in CCl_4 with NaOCl or $NaIO_4$ in water using RuO_2 and Adogen-464 (tetraalkylammonium salt) gave α-tetralone in low yield, rather than the expected product, adipic acid. The two phase oxidation of 1-methylnaphthalene with $NaIO_4$ in the presence of RuO_2 and Adogen-464 gave a good yield of phthalic acid and 3-methylphthalic acid. These were characterized by HPLC analysis of the p-bromophenacyl esters. The more easily oxidized naphthalene rings show greater promise in this type of analysis than the benzene systems.

A number of oxidizing agents are available for oxidation of aromatic hydrocarbons to the aryl ketones and aldehydes. A high yield reaction was desired for use in the quantitative analysis of lignite-derived oils which contain many methyl and other alkylarenes as well as hydroaromatics. HPLC analyses of the oxidation products and their 2,4-dinitrophenylhydrazones were carried out. The oxidation of tetralin to α-tetralone using ceric ammonium nitrate in nitric acid (5) could not be repeated. Instead the nitrate ester of tetralol was obtained. A similar product was reported for o-xylene oxidation (6). Using acetic acid as the solvent (7) produced the acetate ester of α-tetralol. A matrix of conditions was studied utilizing a phase transfer catalyst in the tetralin oxidation to determine maximum yield conditions. Thus a 74% yield of α-tetralone was obtained using a benzene-water system with Adogen-464, with no side reaction products.

Ceric ammonium nitrate oxidation of naphthalenes in two phase systems with Adogen-464 gave naphthoquinones and mixtures of products, thus this oxidizing system will be of limited usefulness in the study of naphthalenic and larger aromatic ring systems.

Adogen-464 was also very effective in catalyzing the oxidation of tetralin in benzene with $KMnO_4$ as the oxidant (8). Thus the "purple benzene" reagent gave a high yield, 90%, of α-tetralone.

Other oxidizing reagents, such as nitrobenzene and peroxydisulfate, which sometimes give aldehydes or ketones, were not successful in the model compound or light oil oxidation studies.

Experimental Section

Trifluoroperacetic acid oxidations were performed as in Reference 1 and excess reagent destroyed with Pt/asbestos. Most of the trifluoroacetic acid was evaporated at low temp/pressure on a rotary evaporator. The pH was adjusted to 6.8 and an equal volume of ethanol was added. The solution was filtered and refluxed with p-bromophenacyl bromide for 15 minutes. The esters were extracted with ethyl acetate and analyzed with an Altex Model 332* liquid chromatograph with u.v. detection.

Ruthenium tetraoxide oxidations were performed by dissolving 0.3 g of organic substrate in 25 ml CCl_4 and adding to 2.0 g $NaIO_4$ in 25 ml water. Adogen-464 (Aldrich) (50 mg) and 20 mg RuO_2 were added and stirring continued overnight. A second 2.0 g of $NaIO_4$ were added and stirred overnight. Acids were extracted from the acidified aqueous layer and analyzed by HPLC after conversion to the p-bromophenacyl esters.

Ceric ammonium nitrate oxidations were performed by adding 10.5 g of the reagent in 40 ml water to 0.3 g organic substrate in 10 ml benzene or other solvent. Adogen-464 was added and the mixture stirred and heated at 60-65° for 3 hrs. A second 10.5 g of reagent in 15 ml water was added and heating continued for 5 hrs. Extraction of the mixture with pentane gave the carbonyl products. Permanganate oxidation was carried out similarily.

* Reference to specific brand names and models is done to facilitate understanding and neither constitutes nor implies endorsement by the Department of Energy.

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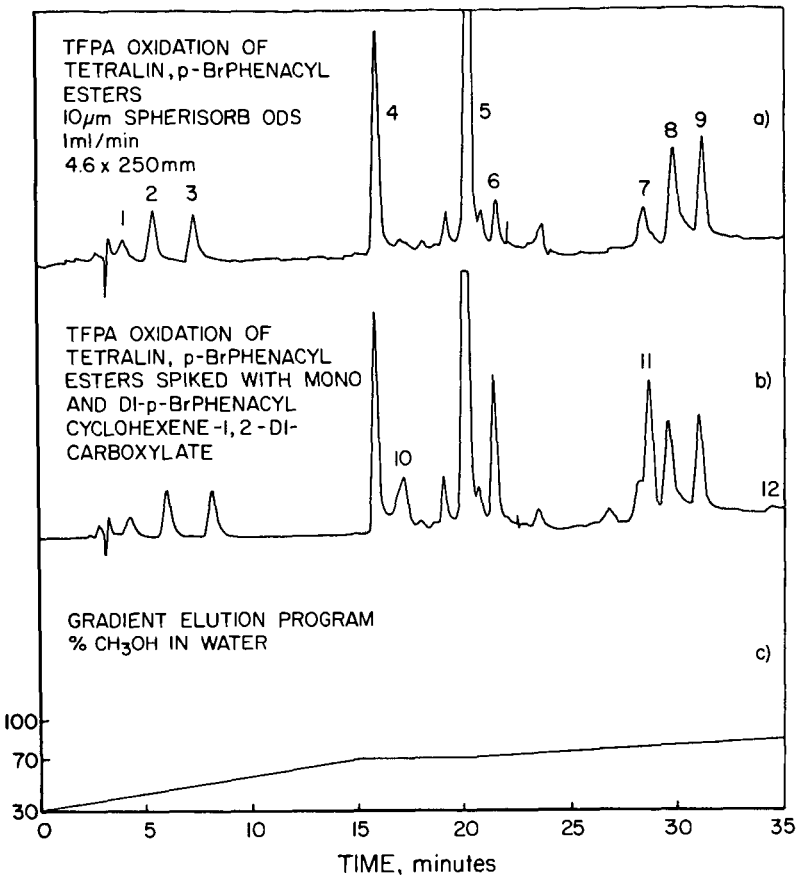

Figure 1. - Separations of p-bromophenacyl esters of tetralin TFPA oxidation products. Peak numbers refer to compounds in Table 1.

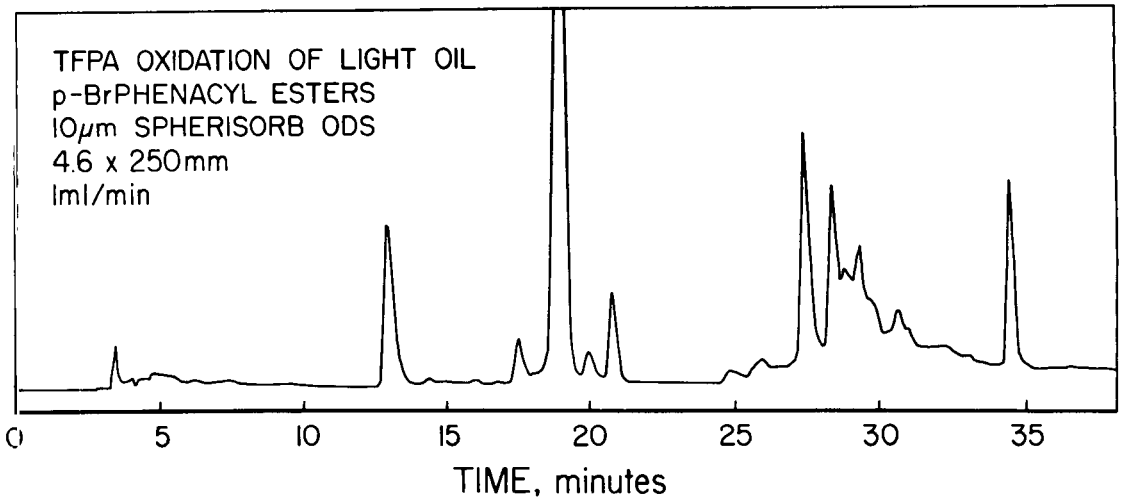

Figure 2. - Separation of p-bromophenacyl esters of light oil TFPA oxidation products.