Transactions of the Illinois Academy of Science
(1985), Volume 78, 1 and 2, pp. 25-28

CYCLIC ANHYDRIDES OF 1,2; 2,3 and 1,8 — DICARBOXYLIC ACIDS OF NAPHTHALENE PRODUCED FROM DICHROMATE OXIDATIONS OF SOLVENT REFINED LIGNITE — A POSSIBLE CLUE TO POLYMER STRUCTURES IN LIGNITE

Robert C. Duty
Chemistry Department
Illinois State University
Normal, IL 61761

ABSTRACT

Solvent refined lignite was oxidized with aqueous sodium dichromate, and produced only three dibasic acids of naphthalene. The total number of dibasic acids of naphthalene are ten, however, only three of these isomers will form cyclic anhydrides (1-2, 2-3, and 1-8 isomers). This study identified the three dibasic acids produced from the oxidation of solvent refined lignite by converting them to their cyclic anhydrides which suggest how the units of naphthalene are connected in lignite structures.

INTRODUCTION

Shechter *et al.* (1965) have shown that aromatic acids can be synthesized in good yields from alkyl substituted aromatic hydrocarbons.

$$\text{2-Methylanthracene} \xrightarrow[250°\text{C}]{\text{aq. } Na_2Cr_20_7} \text{2-Anthracenal carboxylic acid}$$

Hayatsu *et al.* (1975, 1978) have studied the oxidation of coals using aqueous sodium dichromate according to the procedure of Shechter (1965), and have reported an extensive list of condensed ring aromatic carboxylic acids which were identified as the oxidation products from these coal oxidation studies. Hayatsu *et al.* (1978) also reported the results of his basic extraction studies with lignite and reported the following acids; benzene carboxylic acids (16.6%), methylbenzene carboxylic acids (16.0%), phenolic acids (40.0%) furancarboxylic acids (0.8%), aliphatic dibasic acids (10.8%), terpenoid acids (6.6%) benzo and hydrobenzofuran carboxylic acids (4.3%) and unidentified acids (4.5%). It was interesting to note that no acids of naphthalene were extracted with the 2.5% aqueous sodium hydroxide which he used to extract these acids.

Previously we had reported the results of the study of aqueous sodium dichromate on a North Dakota lignite and its solvent refined lignite (Duty, 1980). This study identifies the aromatic cyclic anhydrides of naphthalene from the solvent refined lignite.

MATERIALS AND METHODS

These anhydrides were analyzed by a gas chromatography-time of flight mass spectrometer (GC-TOFMS). The gas chromatograph was a Perkin-Elmer 3920B gas chromatograph interfaced to the TOFMS with a continually variable split between the flame-ionization detector and the source of the mass spectrometer. The GC column was 15.2 m × 0.57 mm support-coated, open tublar column with an OV-17 substrate. Temperatures were programmed from 100°C to 250°C @ 4°C min^{-1}, with helium as the carrier gas. The high-resolution mass spectral data were obtained with an AEI MS-902 using a PDP-8 computer for data reduction. Samples were also run on the TOFMS with a variable-temperature solid inlet (Hayatsu, 1975). The gc retention times for the 1,2; 2,3 and 1,8-dicarboxylic acids of naphthalene were 34.8 min, 38.3 min, and 38.8 min, respectively. Mass spectrometer readings produced molecular ion peaks at 198, base peak at 126 and daughter ion at 162 for each. Standards were run with 1,8-naphthalic anhydride (Aldrich Chem. Co.) and 2,3-naphthalic anhydride produced by refluxing 2,3-naphthalene dicarboxylic acid (Aldrich Chem. Co.) with acetic anhydride. Dipole moments were calculated for 1,8-naphthalic, 2,3-naphthalic, and 1,2-naphthalic anhydrides and were 8.39, 7.44 and 6.47 Debye units, respectively. These dipole moments agreed well with their gc retention times which have been shown to increase with increase in dipole moments for different isomers (Duty, 1977).

These oxidations were carried out on a 10g. sample of solvent refined lignite that had been extracted into a benzene-methanol reflux as previously described (Duty, 1980). The solvent from the benzene/methanol was removed, and the residue was refluxed for 1-2 h with approximately 100 ml of acetic anhydride. The solution was evaporated to dryness, and the residue was dissolved in methylene chloride for GC-MS analysis. The oxidation was carried out at 250° for 72 h with limited dichromate (55.1g $Na_2Cr_2O_7$ H_2O, 500 ml H_2O, 5g. NaH_2 PO_4 H_2O) and analyzed as previously described (Duty, 1980).

RESULTS AND DISCUSSION

In the previous study (Duty, 1980), we had identified naphthalene dicarboxylic acids as one of the most abundant acids produced in the oxidation of the solvent refined lignite. In that study it was apparent from the gas chromatographic traces that the methyl esters of the naphthalene dicarboxylic acids were eluting as only three peaks.

There are 10 isomers for the dicarboxylic acid of naphthalene, and only 3 of these isomers would form cyclic anhydrides; the 1,8, the 1,2 and 2,3 dibasic acids (See Figure 1).

Since the limited dichromate oxidation of SRL produced three naphthalene dibasic acids, the acids from these oxidation reactions were converted to anhydrides by refluxing with acetic anhydride to ascertain if any of these three cyclic anhydrides were present. The results of these anhydride experiments are given in Table I.

The most abundant cyclic anhydride was phthalic anhydride and all of these naphthalene anhydrides have been normalized to phthalic anhydride which was chosen as 100. The interesting feature in Table I is the appearance of all three cyclic anhydrides of naphthalene. The other 7 isomers of naphthalene evidently are not produced or produced in such low percentages that they are not detected by the GC-Mass spectrometer.

These three dibasic acids of naphthalene suggest that the polynuclear aromatic and/or hydroaromatic repeating units in solvent refined lignite extend from the 1,2 position in naphthalene as frequently as they do from the 2,3 position, i.e., a phenanthrene-type repeating unit and/or an anthracene-type repeating unit (See Figure 2).

In addition, since the 1,8-cyclic anhydride represented only about 6-7% of the concentration as the other two cyclic anhydrides, one can conclude that the repeating units which branch off from the 1,8 position of naphthalene are very few compared to the 1,2 and 2,3 positions.

ACKNOWLEDGEMENTS

The author is greatful for a faculty research appointment at the Argonne National Laboratory funded by the Department of Energy, and wishes to express his thanks to R. Hayatsu and R.E. Winans for their helpful discussions.

REFERENCES

Duty, R.C. 1977. Isomer Distribution and Identification for the Chlorination Reaction of Acetylated 3-, 4-, 5-, and 6-Chloro-2-Methylanilines by Gas-Liquid Chromatography. *Anal. Chem. 49*, 743-746.

Duty, R.C., Hayatsu, R., Scott, R.G., Moore, L.P., Winans, R.E. and Studier, M.H. 1980. Characterization of a Complex Mixture of Aromatic and Heterocyclic Acids Obtained from Oxidation of Lignite Coal and its Solvent-Refined Products. *Fuel* 59, 97-101.

Hayatsu, R., Scott, R.G., Moore, L.P. and Studier, M.H. 1975. Aromatic Units in Coal. *Nature 257*, 378-380.

Hayatsu, R., Studier, M.H., Moore, L.P. and Anders, E. 1975. Purines and Triazines in the Murchison Meteorite. *Geochim. Cosmochim. Acta* 39, 471-472.

Hayatsu, R., Winans, R.E., Scott, R.G., Moore, L.P. and Studier, M.H. 1978. Trapped Organic Compounds and Aromatic Units in Coal. *Fuel* 57, 541-547.

Shechter, H., Friedman, L. and Fischel, L. 1965. Oxidation of Alkylarene with Aqueous Sodium Dichromate. A Useful Method for Preparing Mono- and Polyaromatic Carboxylic Acids. *J. Org. Chem. 30*, 1453-1456.

Table I. Relative Abundances of Cyclic Anhydrides (SRL-Benzene/MeOH extract-limited $Na_2Cr_2O_7$ oxidation)

Anhydrides	SRL
Phthalic anhydride	100
2,3-naphthalic anhydride	10
1,2-naphthalic anhydride	9.0
1,8-naphthalic anhydride	0.64

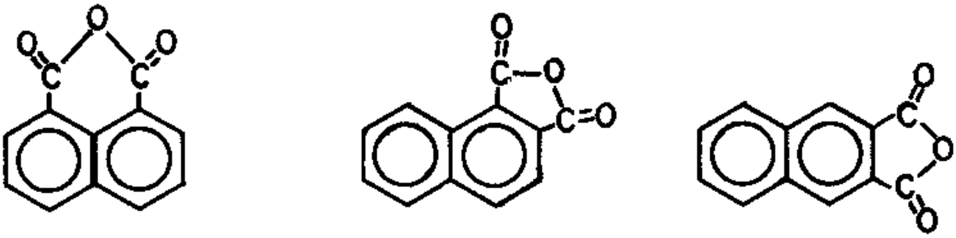
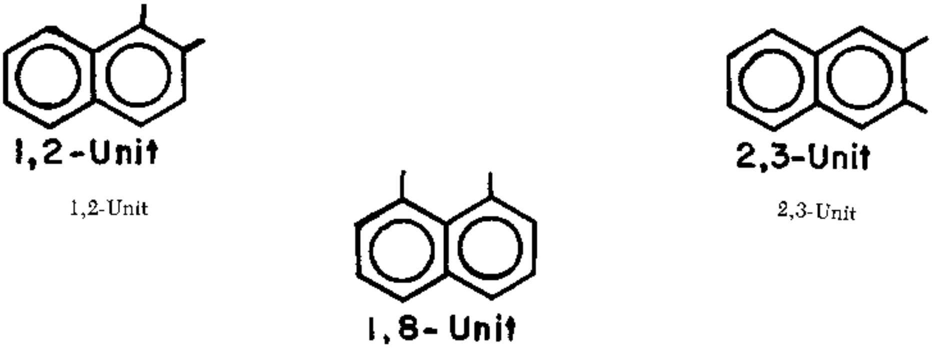


Fig. 1



1,2-Unit

2,3-Unit

1,8-Unit

Fig. 2