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THE SINGLE ELECTRON CHEMISTRY OF COALS

Report for the period
October 1 to December 31 1992

John W. Larsen
and Thomas P. Eskay

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OBJECTIVES AND SCOPE OF WORK

Objectives

To investigate and characterize the single electron reactions of alkyl and alkoxy aromatic compounds in order to determine the role these reactions play in the chemistry of coal.

Scope of Work

1. Attempts will be made to demonstrate that the radicals from inertinite maceral group will initiate the polymerization of 4-vinylpyridine.
2. The molecule, N,N-diphenyl-phenylenediamine, will be deposited in coals to characterize their native free radicals.
3. Tetracyanoquinodimethane (TCNQ) and tetracyanoethylene (TCNE) will be used to characterize the numbers and strengths of single electron donors in coals.

Introduction

Depolymerization of coals at low temperatures may offer advantages over thermal bond cleavage. Because bond cleavage energies of radical cations are lower than the corresponding homolytic bond cleavage energies of the same bond^{1,2}, generation of radical cations in coal may make possible depolymerization at lower temperatures.

We seek to investigate the above possibility using single molecules containing functional groups common in coals. Since the generation of a radical cation requires the removal of an electron from a neutral molecule, a primary focus of the study will be finding oxidants that will remove an electron from compounds with structural similarity to those typically found in coals. The study will also be concerned with the decomposition of radical cations and the products formed as a result of the decomposition.

Results and Discussions

In our last report we described the results of the single electron oxidation of 4,4'-dimethoxybibenzyl (DMBB) with excess $\text{Fe(III)(1,10-phenanthroline)}_3(\text{ClO}_4)_3$ (Fe(III)(PHEN)) in refluxing CH_3CN (82°C).³ Briefly, using a 60 mole % excess of Fe(III)(PHEN) , gas chromatography (GC) product analysis of the reaction mixture revealed a 72 % recovery of starting material, DMBB, and the formation of 6 % (weight %) of the cleavage product p-anisaldehyde.

The mass balance was 77 %, indicating that products were formed in the reaction that were not detected by GC. Because an incomplete mass balance was observed, we have continued our study of this reaction by attempting to identify the additional products formed.

Figure 1

A plasma desorption mass spectrum of the above reaction is shown in Figure 1. Several peaks with m/e ratios $>$ than 300 are present in the spectrum. Control experiments using synthetic reaction mixtures containing the products detected by GC analysis did not contain these peaks. One reasonable assignment for the peaks at m/e 482 and 602, consistent with the known ability of radical cations to undergo substitution reactions, is the dimer and

p-methoxybenzylated dimer of **DMBB** respectively. Fragmentation of the **DMBB** dimer in the mass spectrometer with the loss of a methyl radical or a p-methoxybenzyl radical would give rise to the peaks observed at m/e 467 and 361 respectively (see Figure 2). Alternatively, the peaks at m/e 361, 482, and 602 could be assigned as the mono, di, and tri-p-methoxybenzylated **DMBB**. Structures have not been assigned to other peaks present in the spectrum. The existence of these high molecular weight products explains the incomplete mass balance.

Figure 2

The formation of high molecular weight products in larger amounts than the desired cleavage product, p-anisaldehyde, may be due to an inability of CH_3CN to solvate the **DMBB** radical cation

long enough to allow bond cleavage. To investigate this possibility, oxidations of DMBB using Fe(III)(PHEN) were performed in CH_2Cl_2 and sulfolane. Results of these reactions are given in Tables I and II in the data and results section. Similar to the results obtained in CH_3CN , small amounts of p-anisaldehyde were formed and incomplete mass balances were observed for each reaction. Further investigation of these reactions are currently underway. Attempts to use N,N-dimethylformamide, N,N-dimethylacetamide, and 1-methyl-2-pyrrolidinone as reaction medium were unsuccessful. Reduction of Fe(III)(PHEN) to Fe(II)(PHEN) was observed when the Fe(III) salt was dissolved in each of the three solvents.

Experimental Section

All compounds were commercially available, except for **Fe(III)(Phen)** and **DMBB** (synthesis below), and were used as purchased or repurified as follows. Anhydrous CH_2Cl_2 and *p*-anisaldehyde (Aldrich). Sulfolane and 3-methylsulfolane (Aldrich) were combined in a crimp top vial with 3-methylsulfolane as 5 % of the total weight of the combined compounds. After shaking, a homogeneous liquid was obtained and activated 4 A molecular sieves were added to the vial and the vial was capped and shaken for 2 hours prior to use in reactions. Phenanthrene (Baker) the GC internal standard was recrystallized from absolute ethanol prior to use. **DMBB** and **Fe(III)(PHEN)** were dried to constant weight in vacuum (0.4 torr.) across from P_2O_5 prior to use.

Ultraviolet spectra were obtained on a Perkin-Elmer Lambda 5 UV/VIS spectrophotometer between the wavelengths of 200 and 900 nm. with a slit width of 2 nm. The solvent for both reference and sample was anhydrous acetonitrile using 1 cm. quartz cells.

NMR spectra were obtained on a JEOL FX90Q FT NMR spectrometer.

Plasma desorption mass spectra were obtained on a BIO ION 20.

Iron(III)(1,10-phenanthroline)₃(perchlorate)₃

Iron(III)(1,10-phenanthroline)₃(perchlorate)₃ was prepared by the method described in the previous paper.³ Iron(II) sulfate heptahydrate 1.34 g. (0.0048 moles) and 2.59 g. (0.014 moles) of

1,10-phenanthroline were warmed with stirring in 29 ml. of water. When all the solid had dissolved, the resulting deep red solution was filtered into a flask which was immersed in an ice bath. 7.2 ml. of 1M H₂SO₄ was then added to the solution. After cooling in an ice bath, 4.58 g. (0.019 moles) of lead(IV) oxide was added and the solution was stirred for approximately 10 minutes until all the iron(II) (red) was converted to iron(III) (blue). Excess lead(IV) oxide was filtered off by using a sintered funnel and 1.76 g. (0.014 moles) of sodium perchlorate was added to the filtrate. The solution was stirred and a blue precipitate appeared. The precipitate was filtered and recrystallized from dilute perchloric acid (1:1 v:v). After drying (see above) it was characterized by UV spectroscopy λ_{max} 590 nm. in acetonitrile (lit. 592'). The synthesis was completed as quickly as possible since the complex decomposes in aqueous solution.

4,4'-dimethoxybibenzyl

DMBB was synthesized using a procedure by Trahanovsky⁵. 0.84 g. (0.035 moles) of magnesium and 10 ml. of anhydrous diethyl ether were placed into a flame dried two neck 50 ml. flask under N₂ containing a magnetic stirrbar and equipped with a flame dried addition funnel. A 10 ml. diethyl ether solution containing 10 g. (0.069 moles) of p-methoxybenzyl chloride (Aldrich) was added to the addition funnel and a dropwise addition of the solution was carried out over the period of one hour. The resulting solution was allowed to stir overnight. The reaction was quenched with the dropwise addition of H₂O after which 3 M. HCl was added until the

aqueous layer was acidic to litmus paper. The aqueous layer was extracted with ether (3 X 15 ml.) and a white solid present remained in this layer. The solid was filtered from the ethereal layer taken up in CH_2Cl_2 and filtered to remove residual magnesium salts. The CH_2Cl_2 was removed by rotary evaporation and the solid was recrystallized from absolute ethanol to give 2.1 g. (25%) of product. M.p. 125-127°C (lit.⁶ 125-126°C). NMR (CDCl_3 , TMS internal standard) 7.2-6.95 (m, 4H), 6.9-6.7 (m, 4H), 3.75 (s, 6H), 2.75 (s, 4H).

Reactions DMBB with Fe(III)(PHEN)

The following is a representative procedure. An oven dried 25 ml. two neck flask containing a magnetic stirrer was flushed with N_2 while hot, capped, and cooled to room temperature. the flask was weighed and moved into a glovebox (N_2 atmosphere) where DMBB was placed into the flask. The flask was removed from the glovebox and weighed to give 0.04712 g. (0.194 mmoles) DMBB. The flask was then equipped with an oven dried condenser under N_2 and was wrapped in Al foil. The flask was then charged with 0.5 ml. of sulfolane/ 5% 3-methylsulfolane. A solution containing 0.237 g. (0.264 mmol.) of Fe(III)(PHEN) in 4.5 ml. of sulfolane/ 5% 3-methylsulfolane was then completely transferred to the reaction flask via a transfer needle and the flask was immediately lowered into an oil bath at 86°C and stirring was started. After 2 hrs. the reaction solution was removed from the oil bath. After cooling, 7 drops of saturated aqueous NaHCO_3 was added and the solution was allowed to stir for

0.5 hrs. 0.0516 g of phenanthrene (the internal standard) was added to the solution and the solution was diluted with 15 ml. CH_3CN . A 1 ml. portion of this solution was removed, diluted with 5 ml. CH_3CN , dried over MgSO_4 , and used in the GC analysis.

Chromatography Analysis and Methods

Gas chromatography was carried out using a (10 m. x 0.53 mm. ID) Supelco Nukol column in a Hewlett-Packard 5890 Series II gas chromatograph equipped with an FID detector and on column injector port. The carrier gas was He at a flow rate of 10 cm^3/min . determined at the detector at an oven temperature of 75°C. The analysis was carried out using the following program and an injection size of 0.3 μl .: oven temperature 75°C for 0.5 min., 10°C/min increase to 200°C, 200°C for 35 min. Injector: 75°C for 0.5 min., 40°C/min. to 300°C, 300°C for 15 min. The detector temperature was 250°C.

All reported GC data were response factor corrected using phenanthrene as an internal standard. At least 3 injections of a response factor standard were made for each analysis except where otherwise noted.

Data and Results

Table I. Reaction DMBB with 0.55 equivalents of **FE(III)(PHEN)** in CH_2Cl_2 . 77 % recovery of DMBB after 23 hrs. at reflux. Mass balance 80 %.

Product	Weight %
PA	4 %

Table II. Reaction DMBB with 1.37 equivalents **FE(III)(PHEN)** in sulfolane/ 5 % 3-methylsulfolane. 70 % recovery of DMBB after 2 hrs. at 86°C. Mass balance 71 %.

Product	Weight %
PA	1 %

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