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THE SINGLE ELECTRON CHEMISTRY OF COALS

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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 report³ we described the successful cleavage of benzyl phenyl ether with $\text{Fe(III)(1,10-phenanthroline)}_3(\text{ClO}_4)_3$ (Fe(III)(Phen)) in refluxing acetonitrile (82°C). Having had this success we have extended our study of this reaction to other substrates.

When bibenzyl (BB) was treated with Fe(III)(Phen) in refluxing acetonitrile, no products of C-C bond cleavage β to the aromatic rings were detected by gas chromatography (GC) analysis. A mass

balance of a reaction run for 3 days determined that $98 \pm 2 \%$ (see note a. in data and results section for explanation of error) of the BB was recovered unreacted. The reaction was duplicated in refluxing N,N-dimethylformamide (153°C) and no cleavage products were detected by GC analysis after 47 hours.

Neo-pentylbenzene (NPB) was treated with Fe(III)(Phen) in refluxing acetonitrile. GC analysis of the reaction mixture after 24 hours indicated that $97 \pm 4 \%$ of the neo-pentylbenzene was unreacted. Benzylacetamide (BAC) and an unidentified product was detected in the reaction mixture in small quantities (see Table I in the Data and Results section).

We are currently continuing our study of Fe(III)(Phen) oxidations of aromatic compounds with substrates that have lower oxidation potentials.

Kochi⁴ has recently reported charge transfer complex formation and photoactivated charge transfer from aromatic donors to SnCl_4 . Because low rank coals contain functional groups that should be easily oxidized by a single electron acceptor, an experiment was performed where SnCl_4 was stirred with North Dakota Beulah-Zap

Lignite in tetralin at room temperature for 5 days. The whole coal was then filtered off and extracted with tetrahydrofuran. The weight loss of the whole coal was determined to be 5 % compared to 9 % of a control which was not treated with SnCl_4 . A complete mass balance of the SnCl_4 treated coal has not been determined at this point because volatile tin adducts were lost upon evaporation of solvent from the coal extract. Further analysis of the experiment are currently being carried out.

Experimental Section

All compounds were commercially available, except for Fe(III)(Phen)(synthesis below), and were used as purchased or repurified as follows. Anhydrous acetonitrile, anhydrous N,N-dimethylformamide, anhydrous stannic chloride (Aldrich). Tetralin (Aldrich) was shaken with activated 4A molecular sieves in a sealed vial under N₂ prior to use. Neo-pentylbenzene (Aldrich) was dissolved in anhydrous acetonitrile under N₂ in a crimp top vial containing activated 4A molecular sieves prior to use. Bibenzyl (Aldrich) was recrystallized from ethanol. Both bibenzyl and Fe(III)(Phen) were dried to constant weight in a vacuum (0.4 torr.) across from P₂O₅. North Dakota Beulah-Zap Lignite was an Argonne Premium Coal sample and was dried to constant weight in a vacuum oven at 110°C and was stored in a glovebox N₂ atmosphere prior to use. Phenanthrene (Baker) the GC internal standard was recrystallized from ethanol prior to use. Tetrahydrofuran (Fisher certified grade).

Ultraviolet spectra were obtained on a Perkin-Elmer Lambda 5 UV/VIS spectrometer 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.

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 paper³. Iron(II) sulfate

heptahydrate 1.34 g.(.0048 mol) and 2.59 g.(.014 mol) 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.(.019 mol) 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.(.014 mol) 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} 590nm. in acetonitrile (lit. 592⁵). The synthesis was completed as quickly as possible since the complex decomposes in aqueous solution.

Reactions BB and NPB with Fe(III)(1,10-phenanthroline)₃(ClO₄)₃

The following is a representative procedure. An oven dried two neck 25 ml. reaction flask containing a magnetic stirrbar and fitted with a septum was flushed with dry N₂ while hot, capped and allowed to cool in a desiccator. After cooling, the flask was weighed and moved into a glovebox (N₂ atmosphere). Dry BB was placed into the flask and the reaction vessel was removed from the glovebox and reweighed. It contained 0.0408 g.(2.24 x 10⁻⁴ moles) of BB. It was then equipped with an oven dried condenser, wrapped

in Al foil and placed under an N₂ purge. 1 ml of anhydrous acetonitrile was added to the flask with an oven dried syringe. An acetonitrile solution of Fe(III)(Phen) was prepared in an oven dried crimp top vial with 0.265 g. of dry Fe(III)(Phen) and 2.790 g. of anhydrous CH₃CN. 2.979 g. of this solution was then injected into the reaction vessel with an oven dried syringe and the reaction vessel was immediately lowered into an oil bath at 100°C. The amount of Fe(III)(Phen) added was 0.258 g. (2.89×10^{-4} moles) a 29% molar excess. After 3 days, the reaction flask was removed from the oil bath and 10 drops of saturated aqueous NaHCO₃ was added. The resulting solution was allowed to stir for 15 minutes prior to the addition of MgSO₄.

Prior to gas chromatography analysis, 0.0497 g. of phenanthrene, the internal standard, was added to the reaction mixture and the solution was stirred. 1 ml. of this solution was drawn off and diluted with 16 ml of acetonitrile for GC analysis.

Reactions with NPB were carried out in the same manner except the NPB was transferred to the reaction vessel in an acetonitrile solution prepared as described above.

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 cm³./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 μ l.: 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. Neo-pentylbenzene analysis was performed with the same program times and final temperatures but the starting temperature of both the injector and oven were 65°C. 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.

SnCl₄ Beulah Zap Lignite Experiment

In a glovebox (N₂ atmosphere) dry North Dakota Beulah-Zap Lignite 1.0178 g. was weighed into an oven dried 2 neck 50 ml. flask fitted with a rubber septum and containing a magnetic stirrer. The flask was removed from the glovebox and placed under an N₂ purge. 8 ml. of dry tetralin was then injected into the flask followed by 1.275 g. of anhydrous SnCl₄ (both transferred with oven dried syringes). The slurry was stirred at room temperature for 5 days. The slurry was treated with 2 ml of a 1:1 water: absolute ethanol solution and was allowed to stir overnight. The solid was filtered through a dried preweighed cellulose extraction thimble under an N₂ purge using THF as a solvent to aid in transfer and filtration. The whole coal in the thimble was then extracted in a Soxhlet extractor using THF as the extracting solvent for 5 days.

The extract was combined with the original filtrate and the solvent was evaporated to give a residue. The whole coal was dried to constant weight to determine the weight loss of the coal. Upon evaporation of the SnCl_4 extract (in vacuo) a white solid was observed forming in the vacuum trap. The composition of the solid has not yet been determined but the loss in the vacuum lines prevents a complete mass balance of the experiment. A control experiment was performed for comparison where all conditions and times were the same except SnCl_4 was not added.

Data and Results

Table I. Reaction NPB with Fe(III)(Phen). Analysis after 24 hours at reflux. Reaction mass balance $99 \pm 4 \%$ ^a

Product	Mole %
NPB	98
BAC	1 ^b

- a. Error reported by determining the standard deviation of 3 injections of the same reaction mixture.
- b. Estimated by using a response factor not determined at the time the analysis was performed.

Table II. SnCl₄ treated North Dakota Beulah-Zap Lignite experiment.

	% Weight Loss in Whole Coal	Weight Balance ^c
SnCl ₄ treated coal	5 %	nd
Control	9 %	110 %

- c. Determined by the sum of the whole coal and the extracted residue divided by the amount of starting coal.
- nd. Not determined (see text).

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