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THE SINGLE ELECTRON CHEMISTRY OF COALS

Report for the period
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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

The single electron oxidation of benzyl phenyl ether (BPE) with a molar excess of tris-(1,10-phenanthroline)-iron(III) perchlorate (Fe(III)(Phen)) in refluxing acetonitrile (82°C) produced the products phenol (P), benzyl acetamide (BAC), 2-benzylphenol (2BP), 4-benzylphenol (4BP), and benzaldehyde (BAL) (see reaction 1). The product yields were determined by gas

chromatography (GC) analysis and results are given in Table I. A weight balance revealed that the above products account for $78 \pm 2\%$ of the starting weight of BPE. The incomplete weight balance indicates that products other than those detected by GC were formed in the reaction.

To confirm formation and attempt to identify products not detected by GC analysis, a Plasma Desorption Mass Spectrum (see figure 1.) of a reaction mixture was obtained. Several peaks were present with m/e ratios > 200 . Peaks with m/e 364, 454, and 545 were present. One reasonable family of structures is the dimer of BPE, and the mono and dibenzylated derivatives of this dimer respectively. The dimer structures are shown in figure 2. Another possibility is polybenzylated phenols. Structures have not been assigned to the other peaks. The existence of these high molecular weight products explains the incomplete mass balance. Their existence is consistent with the known ability of radical cations

to undergo substitution reactions.

Figure 1.

The cleavage of BPE by acid has been reported³. It gives the products shown in equation 1 excluding BAL. We confirmed this result by treating BPE with perchloric acid in refluxing acetonitrile (see Table II.). Because the $\text{Fe(III)(1,10-phenanthroline)}_3(\text{ClO}_4)_3$ used in the reactions was recrystallized from perchloric acid (see experimental section), we were concerned that trace acid could be responsible for some of the reaction. Two separate experiments were performed to remove all traces of acid from the Fe(III)(Phen) . Both the solvent and the iron complex were pretreated with either K_2CO_3 or activated alumina prior to being used in reactions (see Tables III. and IV.). In each experiment there was a small decrease in the amount of rearranged products

(2BP and 4BP) formed. Because HClO_4 catalyzed BPE cleavage had a greater yield of rearranged products, this decrease suggests that some acid cleavage was occurring.

Figure 2.

We ultimately want to use the Fe(III)(Phen) catalytically with O_2 as a cooxidant. We previously reported this was achieved by bubbling air through a reaction containing BPE and a catalytic amount of Fe(III)(Phen) ⁴. This reaction was repeated using 29 mole % of Fe(III)(Phen) and a 98.9 ± 0.4 % conversion of BPE occurred after 30 hours. Results of this reaction are in Table V.

Experimental

Materials

All compounds except benzyl acetamide (TCI), phenanthrene (Baker), and benzyl phenyl ether (see synthesis below) were purchased from Aldrich. 4-benzylphenol was recrystallized from n-hexane and phenanthrene was recrystallized from ethanol. All other chemicals were used without further purification. Except for phenanthrene, which gave two small impurity peaks, all compounds used showed only one peak other than solvent in GC analysis.

BPE and Fe(III)(Phen) were dried to a constant weight under vacuum (0.4 torr) prior to use and were stored in a glovebox (N₂ atmosphere).

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

Plasma desorption mass spectroscopy was performed using a Bio Ion 20.

Benzyl Phenyl Ether

Benzyl phenyl ether was synthesized by a modification of a procedure by Pirkle⁵. 5.29 g. (38.3 mmol.) of anhydrous K₂CO₃, 2.7 ml. (30 mmol.) of phenol, and 35 ml. of dried acetone (dried by shaking over CaSO₄ and distilling under nitrogen⁶) were placed into an oven dried, nitrogen purged, three neck 50 ml. flask fitted with a condenser and equipped with a magnetic stirrbar. The resulting mixture was stirred for two hours prior to the addition of 3.8 ml. (34 mmol.) of benzyl chloride. The mixture was then heated to reflux for three days. The reaction solution was filtered,

repeatedly washing the solid with acetone. The filtrate was rotary evaporated to produce a yellow oil, $rf=0.58$ on Baxter MK6F/F254 TLC plates (1:4 CH_2Cl_2 :Petroleum ether b.p. 20-40°C). Flash chromatography of the oil with grade 60 (230-400 mesh) silica gel using the same solvent system given for TLC produced a white crystalline powder which was recrystallized from ethanol twice. Mp 39°C. ^1H NMR 6.8-7.5 (m, 10H), 5.0 (s, 2H). The spectrum agreed well with previous spectra of benzyl phenyl ether.

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 paper⁴. 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 H_2SO_4 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. 592⁷). The synthesis was

completed as quickly as possible since the complex decomposes in aqueous solution.

Reactions BPE 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 was purged 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 BPE was placed into the flask and the reaction vessel was removed from the glovebox and reweighed. It contained 0.0534 g. (2.90×10^{-4} moles) of BPE. It was then equipped with an oven dried condenser and placed under an N₂ purge. An acetonitrile solution of Fe(III)(Phen) was prepared in an oven dried crimp top vial with 0.776 g. of dry Fe(III)(Phen) and 10.558 g. of anhydrous CH₃CN (Aldrich). 4.28 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 0.293 g. (3.28×10^{-4} moles) a 13% molar excess. After 2 hours, the reaction flask was removed from the oil bath and 15 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, 0.0619 g. of phenanthrene, the internal standard, was added to the reaction mixture and the solution was stirred.

Chromatography Analysis and Methods

Gas chromatography was carried out using a (15 m. x 0.25 mm. ID) J&W DB-FFAP column in a Hewlett-Packard 5880A gas chromatograph equipped with a FID detector. The carrier gas was He at a flow rate of 0.5 cm³/min. and the split ratio was 115:1. The column flow rate was determined by a methane injection at 180°C. The analysis was carried out using the following program and an injection size of 0.3 ul.: 180°C for 4.5 minutes, a 10°C/min. temperature increase to 240°C, and 9 minutes at 240°C with the injector temperature at 300°C and the detector at 250°C. The above program and conditions gave the following retention times in minutes: phenol 3.66, benzyl phenyl ether 6.89, benzylacetamide 9.52, phenanthrene 11.33, 2-benzylphenol 14.12, 4-benzylphenol 18.01.

All results were response factor corrected, using phenanthrene as an internal standard, by response factors determined at the time of the analysis. At least 2 response factor determinations were made for each analysis performed. Mass balances were calculated in the following manner using the weights of compounds present in the reaction mixture from GC analysis. Weight of P x 0.991, weight of BAC and BAL x 0.625, weight of 2BP and 4BP x 1. After multiplication the numbers were summed and divided by the original starting weight of BPE to give the mass balance.

Data and Results

Table I. Reaction BPE with molar excess of Fe(III)(Phen). Mass balance from GC analysis 78 ± 2 % (Run 1) and 79.8 ± 0.2 % (Run 2). Complete conversion of BPE observed.

Product	Run 1 (Mole %) ^a	Run 2 (Mole %) ^a
P	52 ± 2 %	57 ± 1 %
BAC	64 ± 4 %	63.4 ± 0.2 %
2BP	17 ± 1 %	16.7 ± 0.1 %
4BP	2 ± 1 %	2.7 ± 0.1 %
BAL	nd	nd

Table II. Reaction BPE with molar excess of HClO₄. 95 ± 5 % mass balance. Complete conversion of BPE observed.

Product	Mole % ^b
P	67 ± 4 %
BAC	65 ± 4 %
2BP	24 ± 1 %
4BP	5 ± 1 %
BAL	nd

Table III. Reaction of BPE with Fe(III)(Phen). Solvent and complex pretreated with K₂CO₃. 70 ± 1 % conversion of BPE. 67 ± 3 % mass balance.

Product	Mole % ^a
P	40.1 ± 0.4 %
BAC	38 ± 4 %
2BP	8 ± 1 %
4BP	1 % ^c
BAL	nd

Table IV. Reaction of BPE with Fe(III)(Phen). Solvent and complex pretreated with Al₂O₃. 90.0 ± 0.4 % conversion of BPE. 76 ± 7 % mass balance.

Product	Mole % ^a
P	58 ± 4 %
BAC	47 ± 1 %
2BP	11 ± 1 %
4BP	1.3 ± 0.2 %
BAL	7 ± 4 %

- a. Standard deviations determined from 3 injections of the reaction mixture.
- b. Standard deviations determined from 2 injections of the reaction mixture.
- c. Only determined from 1 injection.
- nd. Not determined. Conversion to BAL was small.

Table V. Reaction BPE with Fe(III)(Phen). Air bubbled through reaction mixture. 98.9 ± 0.4 % conversion BPE.

Product	Mole % ^a
P	30.5 ± 0.4 %
BAC	37 ± 2 %
2BP	17 ± 1 %
4BP	7.1 ± 0.2 %
BAL	nd

a. Standard deviations determined from 3 injections of the reaction mixture.
 nd not determined for reaction. Conversion to BAL was small.

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