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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

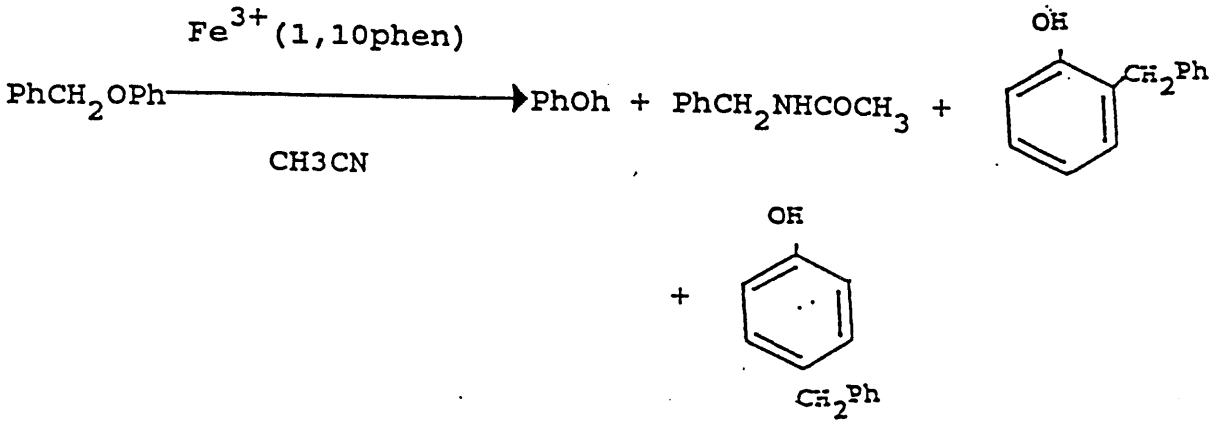
Depolymerization of coals using mild conditions may offer advantages over thermal bond cleavage. Because bond cleavage energies of radical cations are lower than the corresponding homolytic bond cleavage energies of the same bond[1,2], generation of radical cations in coal may offer depolymerization 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 must also be concerned with the decomposition of radical cations.

The work described below is the effort of a new graduate student to familiarize himself with the system and reproduce our earlier results.

Results and Discussions

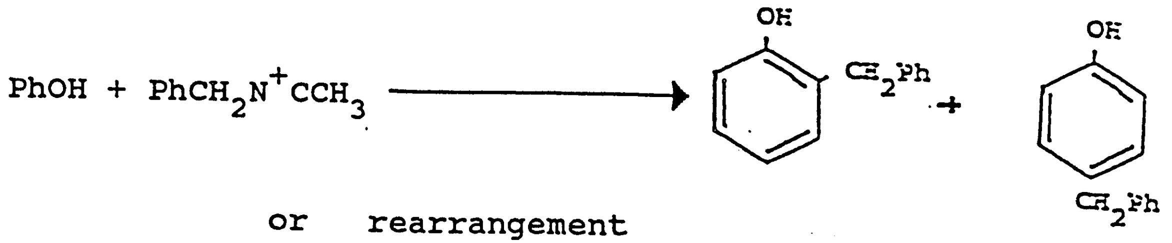
The reaction of benzyl phenyl ether (BPE) with tris-(1,10-phenanthroline)-iron(III) perchlorate in refluxing acetonitrile (see experimental section for details) produced phenol (P), benzyl acetamide (BAC), and two rearranged products, 2-benzylphenol (2BP) and 4-benzylphenol (4BP) (see equation(1)). Because tris-(1,10-phenathroline)iron(III) perchlorate



(1)

is known to be an outer-sphere electron transfer reagent[4,5], the reaction is thought to be initiated by a single electron oxidation of BPE to form the radical cation. The radical cation can then undergo heterolytic bond cleavage of the C-O bond to produce a benzyl cation and a phenyl radical. The cation and radical can then react as shown below in equations 2-5 to give the final reaction products.

$$PhO^{\cdot} \xrightarrow{CH_3CN} PHOH \qquad (2)$$



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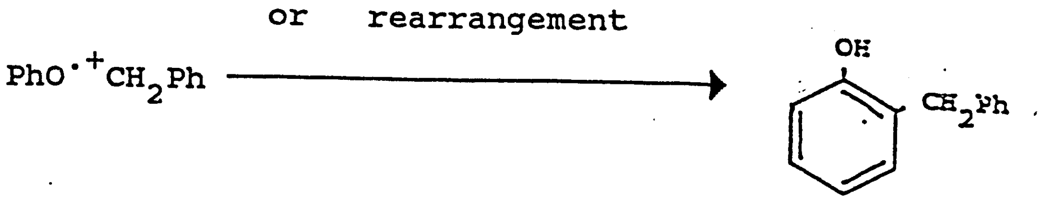


(4)

$$PhCH_2N^+CCH_3 \xrightarrow[NaHCO_3]{H_2O} PhCH_2NHCOCH_3 \qquad (5)$$

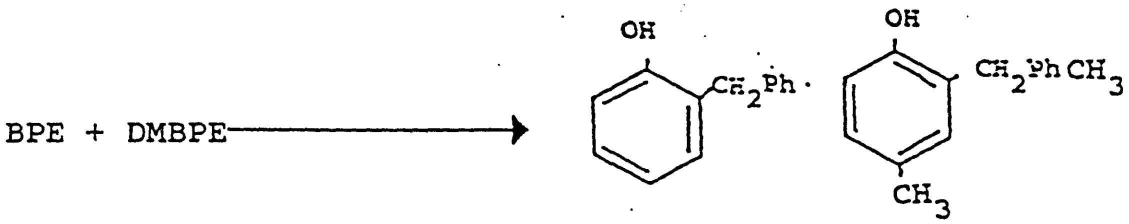
To quantify the above reaction the mass balance must be closed. This requires that the amounts of product formed and starting material remaining can be accurately determined. A number of analytical problems have been encountered which must be solved before we can procede. First, since reaction analysis was performed by gas chromatography (GC) using an internal standard, response factors must be consistent. However, the response factors determined for use in the GC product analysis were inconsistent. The values used with their standard deviations are reported in table I. This problem is due to the solubility of the compounds in acetonitrile and will require a change in reaction solvent. Second, because the final workup volumes were not determined before separating the solutions into several portions, mass balances could not be calculated. Future work will focus on obtaining and closing the mass balance.

Our current work with reaction 1 has shown that after 5 hours at reflux in acetonitrile significant amounts of starting material remain. This result differs from our previous report[3] that all the BPE was converted to products in under two hours. Reaction conditions used in our current work and in our previously reported work were the same. We have not yet determined the reason for the difference in results. One possible explanation is that the iron complex is slowly converting from the iron(III) to iron(II) state in storage. Thus, at the start of the reaction there may not have been enough iron(III) complex to react with all the starting material. This explanation is supported by the following results. During the first 15 minutes of the reaction the ratio of moles of product to moles of starting material was 4.0. After 5 hours only a small amount of additional starting material was converted to products.

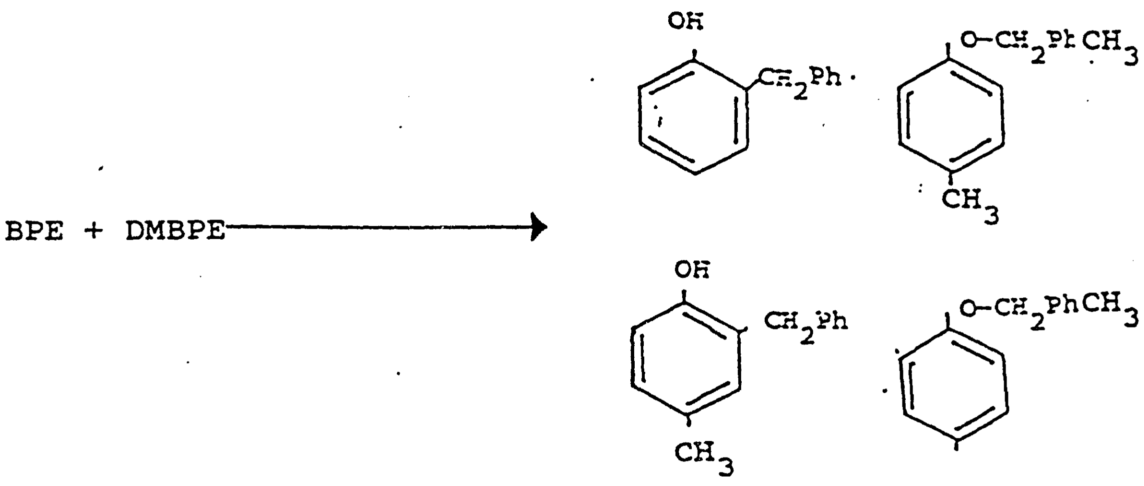
To avoid the problem of not knowing how much of the iron(III) complex is present at the start of a reaction, in the future we intend to store and deliver the iron complex to the reaction mixture in an anhydrous acetonitrile solution. This will allow for an easy measurement of the amount of iron(III) in the solution, by UV spectroscopy, prior to the start of a reaction. Thus, the amount of iron(III) complex in the reaction will be known.

To determine if light has any effect on the reaction, the reaction was repeated in pyrex with no precautions to exclude light. After 3.25 hours, the ratio of moles of product to moles of starting material was 84 (see result tables IV. and V.), greater than that observed in the dark. The larger conversion suggests that light may have effect the reaction. A reaction will be run where the contents of one reaction will be divided into two portions. One portion will be protected from light and one will not. Results of this experiment should indicate whether or not light has an effect on the reaction.

It is not known whether the rearranged product, 2-benzylphenol, is formed by an intramolecular reaction or by an intermolecular reaction. A previous attempt to determine this by a cross reaction with benzyl phenyl ether and p-bromobenzyl-p-bromophenylether failed. The bromo compound did not cleave at the C-O bond (for more detail see ref.3). We intend to try again using the cross reaction with both BPE and 4,4'-dimethyl-benzyl phenyl ether (DMBPE). If the DMBPE reacts in the same way as BPE then we will expect to see the formation of two products, if the reaction is intramolecular (equation 6), or 4 products if the reaction is intermolecular (equation 7).



(6)



(7)

Experimental

Materials

Anhydrous acetonitrile was purchased from Aldrich in a sure seal bottle and used without further purification or drying. The oxidizing reagent iron(III)(1,10-phenanthroline)$_3$ (perchlorate)$_3$ was prepared as described below and its purity was checked by UV spectroscopy. Benzyl phenyl ether was prepared by previous personnel[3] and was a white solid m.p. 38-39°C (lit.[6] 39°C) and ^1H n.m.r ($CDCl_3$) 5.0 (2H, s), 6.8-7.4 (10H, m). Purity was checked by gas chromatography and only one peak was observed except solvent(CH_3CN). Both the iron(III) complex and the benzyl phenyl ether were dried to constant weight under vacuum (0.4 torr) with P_2O_5 as a drying agent, then stored in a dry box.

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

Melting points were obtained using a Meltemp melting point apparatus and are uncorrected. N.M.R. spectra were obtained on a Joel FX90Q FT NMR Spectrometer.

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.(.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 and when cooled to ice bath temperature 4.58 g.(.019 mol) of lead(IV) oxide was added and the solution was stirred 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 l_{max} 590nm. in acetonitrile (lit. 592[7]). The UV spectra also determined the complex to be 97% iron(III) and 3% iron(II) complex from molar absorption data given by Kochi[7]. The synthesis was completed as quickly as possible since the complex decomposes in aqueous solution.

Reactions and Method of Product Analysis

The following is a representative procedure for the reactions. The apparatus, consisting of a two neck 25 ml. Bantam-ware flask, condenser, and magnetic stirring bar, was dried overnight in an oven at 120°C and while hot moved into a dry glove box (nitrogen atmosphere). Benzyl phenyl ether .0585 g. (3.17×10^{-4} mol) and .3292 g. (3.67×10^{-4} mol) of tris-(1,10-phenanthroline)-iron(III) perchlorate were weighed into the flask and the apparatus was assembled and wrapped in aluminum foil. Upon removal from the dry box, the reaction apparatus was placed under a nitrogen purge. 5.8 ml. of anhydrous acetonitrile was then injected into to flask using an oven dried syringe, and the flask was quickly lowered into an oil bath at 110°C.

The reaction was followed by removing 1 ml. of the reaction mixture at intervals and immediately quenching the portion with an equal volume, 1 ml., of saturated aqueous sodium bicarbonate. A dark red upper layer was removed and excess sodium chloride was added to the remaining aqueous layer. The aqueous layer was then extracted with 3 1 ml. portions of methylene chloride, which were added to the first deep red layer removed. The organic layer was then dried over magnesium sulfate.

Product identification and analysis was done by gas chromatography and pure compounds were used to establish the retention times for the products. The final volumes, after workup, of aliquots drawn off reactions were not determined and complete mass balances were not obtained. Results are thus based on the number of moles of product and starting material determined from the GC trace relative to the internal standard, naphthalene. Response factors were determined using pure materials and, on the column used for the analysis, were inconsistent. The response factors and their standard deviations are reported in the data section below (Table I.).

Gas chromatography was carried out using a (15 m. x 0.25 mm. ID) Suppelco SPB-1 column in a Hewlett-Packard 5880A gas chromatograph equipped with a FID detector. The carrier gas was He at a flow rate of 0.6 cm^3./min. and the split ratio was varied from 113-60:1. The analysis was carried out using the following program: 110°C for 6 minutes, a 10°C/min. temperature increase to 200°C, and 5 minutes at 200°C.

Data and Results

Table I. Response Factors (relative to naphthalene as the internal standard using the following equation)

$$RF=\frac{(\text{area of std.})(\text{weight of compound})}{(\text{area of compound})(\text{weight of standard})}$$

Product	Response factor(with std. dev.)
P	1.7 ± 0.2
BAC	3.7 ± 1.0
BPE	1.4 ± 0.1
RP(2BP)	1.4 ± 0.3
RP(4BP)	1.6 ± 0.3

Table II. Ratio of the number of moles of product to moles of starting material for reaction 1.

Time(hrs)	Ratio[a]
0.25	4.0
0.75	2.3
1.75	6.1
5.0	9.4

Table III. Product Yields from reaction 1. (weight%)

P	BAC	RP(2BP)	RP(4BP)
25%	66%	8.0%	1.3%

Table III. Ratio of number of moles of product to moles of starting material for reaction 1 (Reaction not protected from light)

Time(hrs.)	Ratio[a]
0.25	8.3
0.75	12
1.5	19
3.15	84

Table IV. Product Yields from Reaction 1. (Reaction not protected from light) (weight %)

P	BAC	RP(2BP)	RP(4BP)
49%	41%	9.2%	1.1%

[a] The number of moles of P and BAC were added and divided by two. This number was then summed with the number of moles of 2BP and 4BP to give the total number of product moles. The ratio was then calculated by dividing the total number of product moles, calculated as described above, by the number of moles of BPE.

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