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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

Tetracyanoethylene (TCNE) and Tetracyanoquinodimethane (TCNQ) were used earlier in an attempt to determine the single electron donating ability of aromatic groups in coals.^{1,2} The extent of electron transfer from coals to these compounds was measured by determining the frequency shift of the nitrile stretching bands in the Diffuse Reflectance (DR) infrared spectra.³

Our addition to this work will be to study the interactions of coals, such as Illinois No. 6, with TCNE. We will determine whether a Diels-Alder reaction or other addition reactions are occurring.

Results and Discussion

We have previously demonstrated that diffuse reflectance infrared (DRIFT) spectra of the charge transfer complex between TCNE and Illinois No. 6 coal, when heated at 180°C for 7.5 hours and 250°C for 24 hours, do not show the occurrence of any chemical reaction between the coal and TCNE.^{4,5} Because no reaction was observed, we continued this work by studying the reaction between Illinois No. 6 coal and TCNE following the procedures shown by Larsen and coworkers⁶ to result in a Diels-Alder reaction between maleic anhydride and coals.

Reactions of maleic anhydride, a less reactive dienophile than TCNE, with Pittsburgh No. 8 coal have been studied by Quay.⁶ Solid state nuclear magnetic resonance (NMR) spectroscopy demonstrated the occurrence of a Diels-Alder reaction.⁶ The C2 and C3 vinyl carbons of the maleic anhydride shift from approximately 151 ppm to

about 50 ppm (i.e., a sp^2 carbon to a sp^3 carbon). Coupled with a small change for the carbonyl carbon, this result confirms a Diels-Alder reaction.⁶

Figure 1 contains the DRIFT spectrum of the reaction mixture of TCNE and Illinois No. 6 coal. The Illinois No. 6 coal and TCNE were mixed in chlorobenzene, heated at 110 °C for 10 days and then extracted with acetonitrile. Since the position of the nitrile band did not shift to the 2260-2240 cm^{-1} range for non-conjugated CN groups, the double bond remained and a Diels-Alder reaction did not occur.^{7,8} Hence, this is true even at higher temperatures and despite the fact that TCNE is an even more reactive dienophile than maleic anhydride.⁹

By the Woodward-Hoffman rules, a Diels-Alder reaction of the TCNE anion radical is forbidden.¹⁰ By the presence of a transferred electron density in the lowest unoccupied molecular orbital (LUMO) of TCNE from Illinois No. 6 coal, the occurrence of a Diels-Alder reaction is blocked. The LUMO of TCNE remains 30% occupied due to the electron transfer from Illinois No. 6 coal.¹¹ The data shown in this report confirm the possibility of an electron interaction forming extended π structures between Illinois No. 6 coal and TCNE.¹¹

Future work entails plotting the areas under the CN peaks versus time to study the changes in the CN oscillator strengths. Reactions between Pittsburgh No. 8 coal will be reacted with TCNE as previously done with Illinois No. 6 coal.

Figure 1: DRIFT spectrum of the reaction mixture of TCNE and Illinois No. 6 coal.

Experimental

Materials

Illinois No. 6 coal was obtained from the Argonne National Laboratory Premium Coal Sample Program in sealed ampules under a N₂ gas atmosphere. The coal was dried in a vacuum oven at 110°C for 24 hours. Tetracyanoethylene (TCNE) from Aldrich (Milwaukee, WI) was used as received. It was stored in nitrogen filled glovebox to minimize oxidation and hydrolysis. Anhydrous chlorobenzene and acetonitrile from Aldrich (Milwaukee, WI) were used as received. All procedures were performed under a dry nitrogen atmosphere.

Reactions of Illinois No. 6 Coal with TCNE

Approximately 1 g of dried Illinois No.6 coal was weighed into a 3 necked 50 mL round bottom flask and fitted with a thermometer, stirrer bar and a microdistillation head. The flask was removed from the drybox and purged with nitrogen. With a syringe, 25-30 mL of anhydrous chlorobenzene from Aldrich (Milwaukee, WI) was added to the coal. To ensure dryness, a few milliliters of chlorobenzene was distilled off to remove water. No water was visible. After the mixture was cooled and fitted with a reflux condenser, 0.405g of TCNE was added to the coal. The mixture was heated to 110°C and magnetically stirred under dry nitrogen for 10 days. The mixture was filtered through a 10 x 50 mm Whatman Soxhlet thimble at room temperature in a nitrogen filled drybag. The sample was extracted for 3 days with acetonitrile and then dried to constant weight at 60°C in the vacuum oven. Appropriate spectra of the sample were analyzed using Diffuse Reflectance FT-IR.

IR Analysis and Methods

Sample preparation¹² for infrared studies was carried out in a N₂-filled drybox. It involved pre-grinding 300 mg of TCNE-Illinois No. 6 coal sample and KBr in a Wig-L-Bug for 3 minutes. The complex (0.023 g) and KBr (0.743 g) were co-ground for an additional 3 minutes to make a 3.0% mixture. The sample was transferred to the diffuse reflectance cell and leveled with a spatula. The cell was removed from the vacuum atmosphere drybox, placed in the Mattson FT-IR, and appropriate spectra were recorded.

Diffuse reflectance infrared analysis was performed using a Mattson Polarus Fourier transform infrared spectrometer equipped with a 2-dimensional Harrick Scientific Praying Mantis Diffuse Reflectance Attachment. The software used was Enhanced FIRST by Mattson Instrument Inc. Using a deuterated triglyceride sulfate detector, spectra were recorded with 500 scans at 4 cm⁻¹ resolution against a KBr background.

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