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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

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

Figure 1 contains the DRIFT spectrum of the TCNE-Illinois No. 6 coal complex at room temperature. Figure 2 contains the DRIFT spectra of the same TCNE-Illinois No. 6 coal complex after 24 hours at 250 °C. Earlier reports explained that the absence of any significant shift in the peak frequency leads us to believe that the expected Diels-Alder products were not formed.⁴⁻⁶ Initial studies showed a decrease in absorbance at the 2200 cm⁻¹ nitrile peak after 24 hours of heating at 250 °C. Figure 3 contains a plot of the nitrile peak area vs. time. It demonstrates a time dependent loss of the nitrile peak during heating. This result indicates that at 250 °C, which is over the point of sublimation (120 °C), it is very likely that the TCNE is lost from the sample by entering the vapor phase.⁷

The experiment was repeated by doping Pittsburgh No. 8 coal

with TCNE and heating the sample to 250 °C during IR analysis. Figure 4 contains the DRIFT spectrum of the TCNE-Pittsburgh No. 8 coal complex at room temperature. Figure 5 contains the DRIFT spectrum of the complex after 24 hours at 250 °C. The nitrile peak is still located at 2200 cm^{-1} and only a decrease in absorbance still occurs.

It was stated in previous reports that the occurrence of a Diels-Alder reaction would shift the nitrile peak to 2260-2240 cm^{-1} range for a saturated alkyl nitrile.^{8,9} The data in this report indicate that this did not occur. Instead, there is transfer of electron density from the coal to the lowest unoccupied molecular orbital (LUMO) of TCNE. The LUMO of TCNE remains 30% occupied due to the electron transfer from the Pittsburgh No. 8 coal and the occurrence of a Diels-Alder reaction is blocked.⁶

Experimental

Materials

Coals were obtained from the Argonne National Laboratory Premium Coal Sample Program in sealed ampules under a N_2 gas atmosphere. Illinois No. 6 coal and Pittsburgh No. 8 coal were 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. HPLC grade pyridine from Aldrich was transferred to a 250 mL Erlenmeyer flask, placed over potassium hydroxide, and purged with N_2 for 1 hour before sealing

with a septum. All procedures were performed under a dry N_2 atmosphere.

Deposition of TCNE on Argonne Premium Coals

In a Vacuum Atmosphere drybox, 1.30 g of TCNE was weighed into a preweighed 250 ml flask and sealed with a septum. Illinois No. 6 coal (128 mg) was added to a preweighed test tube. A magnetic stirrer was added to the tube and sealed with a septum. The test tube and flask were removed from the drybox to a hood. With a syringe, 50 ml of pyridine was added to the TCNE to make a 0.16 M stock solution. The solution was stirred until all the TCNE was dissolved. With a syringe, 5 ml of stock solution was added to the coal. For 24 hours, the mixture was stirred under N_2 . The sample was then dried in the vacuum at room temperature until it reached constant weight. This procedure was repeated using Pittsburgh No. 8 coal.

IR Analysis and Methods

Sample preparation¹⁰ for infrared studies was carried out in a N_2 -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.

Reactions During IR Analysis

Some reactions were attempted in the diffuse reflectance cell during IR analysis. Spectra were obtained at room temperature and at $250\text{ }^{\circ}\text{C}$ after 24 hours. The diffuse reflectance cell thermocouples were attached to a Model 49 a Proportioning Controller from Love Control Corporation to monitor the temperature in the sample cup inside the diffuse reflectance cell.

Figure 1. DRIFT spectrum of the TCNE-Illinois No. 6 coal complex at room temperature.

Figure 2. DRIFT spectra of the same TCNE-Illinois No. 6 coal complex at 250 °C after 24 hours.

Plot of Area of TCNE Nitrile Peak
vs. Time (hours)

Figure 3. Plot of the nitrile peak area vs. time (hours).

Figure 4. DRIFT spectrum of the TCNE-Pittsburgh No. 8 coal complex at room temperature.

Figure 5. DRIFT spectrum of the TCNE-Pittsburgh No. 8 coal complex at 250 °C after 24 hours.

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