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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.

Experimental

Materials

HPLC grade pyridine (Aldrich) was dried over potassium hydroxide overnight and purged with dry nitrogen before sealing with a septum. Illinois No. 6 coal from the Argonne premium coal bank was dried in a vacuum oven at 110°C for 24 hours and transferred to a N₂-filled drybox. Potassium bromide (KBr) (Fischer) was dried at 450°C in vacuum for two days, sealed and transferred to the drybox. Tetracyanoethylene (TCNE) was transferred to the drybox and used as received.

Deposition of TCNE on Argonne Premium Illinois No. 6 coal

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.

Preparation of Physical Mixture for IR analysis

Sample preparation⁴ was carried out in a N_2 -filled drybox. It entailed pregrinding 300 mg of TCNE-Illinois No. 6 coal complex and KBr in a Wig-L-Bug for 3 minutes. The complex (0.023 g) and KBr (0.743 g) were coground for an additional 3 minutes making a 3.0% mixture. The sample was transferred to the Harrick cell and leveled with a spatula. The cell was removed from the drybox, placed in the Mattson FT-IR, and appropriate spectra were recorded.

IR Analysis and Methods

Diffuse Reflectance infrared analysis was performed using a Mattson Fourier transform infrared spectrometer in conjunction with a 2-Dimensional Harrick Scientific Praying Mantis Diffuse Reflectance Attachment (DRA). The software used was Enhanced FIRST by Mattson Instrument Inc. The Harrick cell thermocouples were attached to a Model 49 Proportioning Controller from Love Control Corporation. During IR analysis, the TCNE-Illinois No. 6 coal

reaction mixture was heated from room temperature to 180°C within the Harrick cell for 7.5 hours. All spectra were obtained using 1000 scans at 4 cm⁻¹ resolution.

Results and Discussion

In our last report,⁵ we demonstrated that the DR spectrum of the charge transfer complex, TCNE-Illinois No. 6 coal, at room temperature does not show evidence for any chemical reaction between the coal and TCNE. At the present, it is established that there has been 69% electron density transfer from Illinois No. 6 coal to the TCNE's lowest unoccupied molecular orbital (LUMO)^{3,6} calculated from the shift in the CN stretching frequency in the spectrum shown in Figure 1. Since no chemical reaction was observed, we continue this study by heating the complex from room temperature to 180°C during IR analysis to see if Diels-Alder or other addition reactions occurred.

While heating the complex for 7.5 hours from room temperature to 180°C, the DR spectrum of the complex displayed no change in the extent of charge transfer as shown in Figure 2: The position of the nitrile band did not shift. Because of this result, a Diels-Alder reaction or other addition reactions are not possible in Illinois No. 6 coal even at higher temperatures and despite the fact that TCNE is an excellent dienophile.⁷

The occurrence of a Diels-Alder reaction would produce CN groups which are not conjugated to a double bond. These non-conjugated CN groups have stretching frequencies between 2260 cm⁻¹ and 2240 cm⁻¹.^{8,9} There are no bands in this region of the IR

spectrum found; therefore, an addition reaction has not occurred nor has any reaction which produces a non-conjugated CN.

The data obtained confirms that the TCNE's LUMO was still occupied 2/3 of an electron transferred by Illinois No. 6 coal. A Diels-Alder reaction of the TCNE radical anion is forbidden by the Woodward-Hoffman rules. It is reasonable that the presence of a transferred electron density in the LUMO is sufficient to block occurrence of this reaction. The data is consistent with the existence of extended π structures in Illinois No. 6 coal; an electron transition occurs within the IR frequency range.¹⁰

Further analysis will be carried out. The sample will be stirred for 1 week instead of 1 day and the complex will be examined by DR infrared analysis after 24 hours at 250°C.

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Figure 1: DR spectrum of TCNE-Illinois No. 6 coal reaction mixture at room temperature

Figure 2: DR spectrum of TCNE-Illinois No. 6 coal reaction mixture at 180°C.

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