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THE SINGLE ELECTRON CHEMISTRY OF COALS

Report for the period
July 1 to September 30 1993

John W. Larsen
and Stephanie E. Rothenberg

Department of Chemistry
Lehigh University
Bethlehem, PA 18015

PREPARED FOR THE UNITED STATES DEPARTMENT OF ENERGY

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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

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. Tetracyanoethylene (TCNE) was transferred to the drybox and used as received. HPLC grade pyridine (Aldrich) was dried over potassium hydroxide overnight and purged with dry nitrogen before sealing with a septum. Potassium bromide (KBr) (Fisher) was dried at 450°C in vacuum for two days, sealed and transferred to the drybox.

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 for 24 hours at 250°C. All spectra were

obtained using 1000 scans at 4 cm^{-1} resolution.

Results and Discussion

We have previously demonstrated that the DR spectrum of the charge transfer complex, TCNE-Illinois No. 6 coal heated from room temperature to 180°C for 7.5 hours does not show the occurrence of chemical reaction between the coal and TCNE.⁵ Because no chemical reaction was observed, we continued this study by stirring the mixture for 1 week and heating the complex at 250°C for 24 hours during IR analysis to see if Diels-Alder or other addition reactions occurred.

Figure 1 displays the DR spectrum of TCNE-Illinois No. 6 coal at room temperature. 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) calculated from the shift in the CN stretching frequency.^{3,6,7}

Figure 2 displays the DR spectrum of TCNE-Illinois No. 6 complex at 250°C for 24 hours during IR analysis. Even if the sample is heated for an extended period of time, the position of the nitrile band did not shift. The data confirms Diels-Alder reaction or the addition reactions were not possible in Illinois No. 6 coal at high temperatures and despite the fact that TCNE is an excellent dienophile.⁸

If a Diels-Alder reaction occurred, the CN peak would have shifted to the $2260\text{--}2240\text{ cm}^{-1}$ range.^{9,10} A Diels-Alder reaction of the TCNE radical anion is forbidden by Woodward-Hoffman rule and the TCNE's LUMO remains 2/3 unoccupied of an electron transferred

from Illinois No. 6 coal.

Once again it is reasonable to say that the occurrence of a Diels-Alder reaction is blocked by the presence of a transferred electron density in the LUMO of TCNE. Extended structure in Illinois No. 6 coal with TCNE exist since an electron transition occurs with the IR frequency range.⁷

Two particular peaks located at 2338 and 2363 cm^{-1} were observed in the heated coal samples. These peaks are caused by coal decarboxylation when heating the sample.¹¹ It is possible low rank coals are susceptible to decarboxylation under slightly elevated temperature.¹¹

Future work will entail looking for changes in the 2000 cm^{-1} to 600 cm^{-1} region in samples such as raw Illinois No. 6 coal, coal soaked in pyridine for a week, and TCNE-Illinois No. 6 coal complex at room temperature and 250°C for 24 hours. The areas under the CN peaks will be plotted as a function of time to study the oscillator strengths in the experiment. Other reactions may be prepared using another solvent, such acetonitrile, to see what effect the pyridine may have on the IR spectra. Furthermore, the reaction of Illinois No. 6 and TCNE will be prepared like the coal reactions done by Quay¹² to see if Diels-Alder reactions or other addition reactions may occur and will be examined using DR-FTIR.

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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 after 24 hours of heating at 250°C.

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