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THE SINGLE ELECTRON CHEMISTRY OF COALS

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John W. Larsen
and Stephanie E. Rothenberg

Department of Chemistry
Lehigh University
Bethlehem, PA 18015

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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 possible chemical reaction of coals with TCNE, especially to detect Diels-Alder products if formed.

The chemistry of TCNE has been thoroughly reviewed, so a detailed discussion is unnecessary.^{4,5} TCNE undergoes a variety of reactions including addition, displacement and cyclization reactions.^{5,6,7} As a reactive dienophile, TCNE readily undergoes Diels-Alder addition reactions with conjugated dienes such as anthracene.⁸

Aromatic molecules and TCNE form complexes in which the TCNE is an electron acceptor.^{6,7} The polyaromatic PNA systems in coals co-operatively transfer a large amount of charge from the PNAs to TCNE.²

Using Diffuse Reflectance FTIR, the extent of charge transfer of TCNE with coal were studied by Flowers.³ Flowers observed a 36 cm^{-1} shift to 2200 cm^{-1} for the nitrile band of TCNE-coal complexes. He reported 2236 cm^{-1} as the CN stretching frequency for TCNE as assigned by Moore et. al. (1971) and Rosenberg et. al. (1965).^{3,9,10} This band is the average of the three symmetrical peaks for TCNE. This peak was not used to calculate the extent of

charge transfer from the DR spectrum of TCNE deposited in Illinois No. 6 coal because the peaks disappear upon charge transfer. Flowers used the 2229 cm^{-1} band in neutral TCNE as the value of the CN stretching band in calculating the extent of charge transfer. Assuming there is a linear relationship between the extent of charge transfer and CN stretching frequency, Flowers observed a 69% charge transfer to TCNE.^{9,11}

Experimental

Preparation of Chemicals and Reagents

Potassium bromide (KBr) was dried at 450°C in vacuum for two days, sealed and transferred to a N_2 -filled drybox. HPLC grade pyridine (Aldrich) was dried over potassium hydroxide overnight and purged with dry nitrogen before sealing with a septum. TCNE (Aldrich) was transferred to a Vacuum Atmosphere N_2 -filled drybox. 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 the drybox.

Preparation of Physical Mixture for IR analysis

Sample preparation was carried out in a N_2 -filled drybox.¹² The preparation entails separately grinding 300 mg of Illinois No. 6 coal and KBr in a Wig-L-Bug for 3 minutes. Grinding longer than 3 minutes does not significantly affect the observed peak intensities.

Illinois No. 6 (0.023g) and KBr (0.743g) were cogrinded for an additional 3 minutes to make a 3.0% mixture. The sample was

transferred to a Harrick cell and leveled with a spatula. The cell was removed from the drybox, and placed in the Mattson FT-IR, and appropriate spectra recorded.

Deposition of TCNE on Argonne Premium Illinois No. 6 Coal

The TCNE was transferred to a Vacuum Atmosphere drybox, 1.30g was weighed into a preweighed 250 ml flask, and sealed with a septum. The flask was removed from the drybox to a hood. With a syringe, 50 ml of pyridine was added to the TCNE making a 1.56×10^{-1} M stock solution. The solution was stirred until all the TCNE dissolved. 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 was removed from the drybox to a hood. Approximately 5 ml of the stock solution was added to the coal via syringe. The mixture was stirred for 24 hrs. under static N_2 . The sample was dried in a vacuum oven at room temperature until it reached constant weight (138 mg). In the drybox, the sample was placed in the sample cup of the Harrick cell and leveled with a spatula. The Harrick cell was transferred out of the dry box to on the Mattson FT-IR.

IR Analysis and Methods

Diffuse Reflectance (IR) spectra were obtained on a Mattson Fourier transform infrared spectrometer equipped with a 2-Dimensional Harrick Scientific Praying Mantis Diffuse Reflectance Attachment (DRA). Enhanced FIRST software by Mattson Instruments Inc. was used. The analysis was carried out using 1000 scans at 4

cm⁻¹ resolution with a scan time of 8.39 minutes for all spectra. For the coal spectrum, 4000 scans were used at 8 cm⁻¹ resolution with a scan time of 20.25 minutes.

Results and Discussion

Figure 1 displays the Diffuse Reflectance Fourier Transform IR (DRIFT) spectrum of Illinois No. 6 coal. The spectrum is similar to spectra of other bituminous coals.^{3,13,14} Briefly, the bands in the 3030-2940 cm⁻¹ regions are due to the aromatic and aliphatic C-H stretch. The 3300 cm⁻¹ band is due to associated OH and NH groups. An intense band at 1600 cm⁻¹ is assigned to aromatic rings. Other bands are due to aliphatic CH₂ and CH₃ groups and aromatic hydrocarbons along with intense mineral bands can be found between 1600 cm⁻¹ to 600 cm⁻¹.

Figure 2 displays the DRIFT spectra of TCNE. The nitrile bands are located at 2262 cm⁻¹, (combined symmetric and antisymmetric modes), and 2229 cm⁻¹ (symmetric mode) and are narrow and sharp. These values match the vibrational frequencies observed by Miller et. al. (1964) and Takenaka et. al. (1964).^{15,16}

Figure 3 shows a DRIFT spectrum of a physical mixture of TCNE and Illinois No. 6 coal. This spectrum was recorded to see if a reaction could occur between TCNE and coal in the absence of a solvent. There is no evidence of reaction: the nitrile band frequencies are identical to those of pure TCNE.

Figure 4 displays the DRIFT spectrum of the room temperature

reaction mixture of TCNE in Illinois No. 6 coal. The nitrile band of TCNE is shifted upfield 29 cm^{-1} from 2229 cm^{-1} to 2200 cm^{-1} providing evidence for a partial charge transfer from coal to TCNE. If a Diels-Alder product formed, we would expect the position of the nitrile group to have shifted to the 2260-2240 cm^{-1} range for a saturated alkyl nitrile.^{17,18} There are no peaks in this region and no evidence for any chemical reactions between the coal and TCNE.

Conclusion

Following the position of the nitrile band and using the assumption that there is a linear relationship for between the extent of charge transfer and frequency, a 69% charge transfer was obtained and successfully replicates Flowers' results. If a Diels-Alder reaction occurred, we would expect the position of nitrile group to have shifted down field to the 2260-2240 cm^{-1} range for a saturated alkyl nitrile.^{17,18} There is no evidence for this type of reaction under these conditions since we obtained a shift upfield from 2229 cm^{-1} to 2200 cm^{-1} .

There are some peaks of interest in the 1660-1300 cm^{-1} range of the deposited coals which will be investigated. The TCNE-Illinois No. 6 reaction mixture will be heated from room temperature to 180°C within the Harrick cell during IR analysis to see if a Diels-Alder or other additions reaction could occur.

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Figure 1: Diffuse Reflectance Spectra of Illinois #6.

Figure 2: Diffuse Reflectance Spectra of TCNE

Figure 3: Diffuse Reflectance Spectra of the physical mixture of TCNE and Illinois #6.

Figure 4: Diffuse Reflectance Spectra of reaction mixture of TCNE and Illinois #6.

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