QUARTERLY TECHNICAL PROGRESS REPORT

for period 1/1/96 to 3/31/96

on DOE/PETC Grant No. DE-FG-22-93PC93218

“Photochemical Coal Dissolution”

David C. Doetschman, Principal Investigator

Department of Chemistry, State University of New York
Binghamton, NY 13902-6016

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
As mentioned in the report on the previous quarter, we have turned our attention to studies of photochemically-induced-charge-transfer phenomena involving aromatic electron donors. Coal is a porous material and it has been demonstrated that there are ground-state charge-transfer-interactions between imbibed TCNE or TCNQ and the aromatic systems in bituminous coals.\textsuperscript{1} We aim to develop a preliminary understanding of the ground and excited state donor-acceptor interactions and the charge-transfer phenomena in porous materials that are better-defined than coals. We are performing background examinations of a set of donors and acceptors in solution by cyclic voltammetry and u.v.-visible spectroscopy. These preliminary experiments are being followed by systematic studies of the adsorption of the donors and acceptors, individually and together into adjacent supercages of a series of cation-exchanged X- and Y-type faujasite zeolites. Ultraviolet-irradiation of these systems are being performed and electron paramagnetic resonance examination of the samples is being made for the presence of paramagnetic, one-electron, charge-transfer products. In related work performed by students supported by this contract, we have reached a good understanding of the interactions and molecular motions of free radical π electron systems in the X- and Y-type faujasite zeolites.\textsuperscript{2,3} Luminescence spectroscopy may also be used to examine the doped zeolite samples in future experiments.

We have begun to examine the donor-acceptor pairs: diphenylamine-benzophenone, nitroxyl and substituted nitroxy radical-benzophenone, and aromatic hydrocarbon-unsaturated tetrycyano hydrocarbon. The oxidation and reduction potentials (vs S.C.E.) and excitation energies of these systems, measured by cyclic voltammetry and u.v.-visible absorption spectrometry in acetonitrile solvent are given in Table 1 and Table 2, respectively. The aromatic hydrocarbon donors span the range of typical aromatic ring sizes found in bituminous, subbituminous and lignite coals. Figures 1 and 2 show typical cyclic voltammetry traces for the electron donors and acceptors.

Figure 3 shows a plot of the oxidation potentials of the aromatic compounds versus the energy of the charge-transfer band energy measured in acetonitrile. Linear extrapolation to zero transition energy gives an oxidation potential of 0.179 ± 0.060 V. In comparison with the reduction potential of TCNE, this implies that the lowest unoccupied molecular orbital (LUMO) of TCNE is poised close to the center of the band gap for extended conjugated aromatic systems. An equally good linear correlation between the $E_{1/2}^{ox}$ versus ΔE for the aromatic hydrocarbons in Table 1 is found, where ΔE is a direct measure of the HOMO-LUMO gap. This is in agreement with early studies of this kind on aromatic ring systems in solution.\textsuperscript{4,5} It also appears to explain the enhancement of the operation of graphite electrodes that can be achieved with TCNE or TCNQ impregnation. It does not appear to explain why TCNE impregnated bituminous coals, which contain relatively small condensed aromatic ring systems, exhibit factors of 10-15 times greater electron delocalization onto TCNE than with molecules of aromatic ring clusters comparable with...
those in bituminous coals.\textsuperscript{1} One possibility is that the electron donating aliphatic functional groups, such as the methyl group, may move the band gap up\textsuperscript{4,5} to better match the TCNE LUMO. Alternatively functional groups in the coal containing occupied non-bonding orbitals, like reported for amines,\textsuperscript{4} may match the TCNE LUMO in energy and result in significant electron delocalization onto TCNE. Experiments with diphenylamine may shed some light on this possibility.

The cation-exchanged zeolite offers an environment in which the cations of the supercage can undergo differential interactions with the donor and acceptor. Previous studies\textsuperscript{2,3} have shown that an occupied (donor) $\pi$ orbital of an aromatic species interacts with the cations of the zeolite supercage. Interaction strengths were of the order 900-1400 cm$^{-1}$. This type of interaction is likely to be different for one type (e.g. donor) organic molecule supercage occupant than another (e.g. acceptor). Thus the zeolite “solvent” environment is a convenient one in which to “solvent-shift” donor and acceptor energy levels in new ways. This altered environment can promote new thermal and photochemical charge-transfer phenomena. The new phenomena will clarify the basic nature of the systems under study and will help understand the course of charge-transfer phenomena in coal pores.

We have begun zeolite cage loading studies on the donors and acceptors in Tables 1 and 2. Some studies of the donor-acceptor pairs has begun. It is well-known that the aromatic hydrocarbon donors can be loaded into zeolite supercages. We have also loaded all of the other electron donors in Table 1 by themselves into the zeolite supercages. Their EPR spectra have been examined before (i.e. the TEMPO compounds), during and after a test irradiation of the species with u.v.-visible light from a high-pressure Hg-Xe arc lamp. In no case is the species chemically photosensitive. Likewise, the acceptors have been loaded into the zeolite supercages and benzophenone has been checked for photochemical reaction on its own. No photosensitivity was exhibited.

The TEMPO compound donors and the benzophenone acceptor have been simultaneously doped into the zeolite supercages. Experiments are continuing in order to ascertain whether the pairs occupy the same or separate supercages and to force single molecule occupancy of adjacent cages experimentally. These donor-acceptor pairs undergo no thermal or photochemical reaction nor do the TEMPO compounds exhibit any differences in EPR spectra over a wide range of temperatures than when adsorbed without benzophenone present. The latter suggests that single molecule occupancy is prevailing.

When the donor-acceptor pair, diphenylamine-benzophenone, are introduced into the zeolite together, an EPR spectrum appears. The spectrum recorded in the Na-X zeolite is shown in Figure 4. It bears repeating that the spectrum does not appear in the absence of benzophenone. Careful work under yellow, clean-room conditions indicates that the spectrum is not being generated inadvertently by exposure to light. The system does not undergo further photochemical
transformations. The hyperfine structure appears to be that of the $^{14}\text{N}$ nucleus suggesting that the radical may be the diphenylamine cation. The intensity of the spectrum is weaker in the Li-exchanged zeolite than in the Na- and K-exchanged X-type faujasites, which exhibit comparable intensities. Rb- and Cs-exchanged zeolites will be examined in order to understand the role that the cation sites may play in the formation of the radical. We have prepared N-deutero-diphenylamine in order to examine the deuteration changes, if any, in the EPR spectrum. The spectrum exhibits a decrease in the major $^{14}\text{N}$ nuclear hyperfine coupling constant with increasing temperature. This is either from an increasing electron withdrawal from the diphenylamine cation with temperature or increased molecular libration or rotation with temperature. The latter is felt to be the more likely reason.

Further experiments on this system will be done to gain a more complete understanding of the nature of the systems. We will also begin to examine the aromatic-tetracyanohydrocarbon systems in the next quarter.

References


DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
Table 1. Oxidation potentials and excitation energies of the electron donor systems being investigated in this study, measured by cyclic voltammetry in acetonitrile solvent referenced to standard calomel electrode (S.C.E.) and by u.v.-visible absorption spectrometry, also in hexane.

<table>
<thead>
<tr>
<th>Donor</th>
<th>$E_{1/2}^{ox}$ (V)</th>
<th>$\Delta E/\hbar c$ (d) (cm)$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthracene</td>
<td>1.09$^{(c)}$</td>
<td>26,700</td>
</tr>
<tr>
<td>Benzene</td>
<td>2.30</td>
<td>38,400</td>
</tr>
<tr>
<td>Diphenylamine</td>
<td>0.886</td>
<td>35,461</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>1.54$^{(c)}$</td>
<td>32,200</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>1.50$^{(c)}$</td>
<td>28,900</td>
</tr>
<tr>
<td>Pyrene</td>
<td>1.16$^{(c)}$</td>
<td>26,900</td>
</tr>
<tr>
<td>TEMPO$^{(a)}$</td>
<td>0.593</td>
<td>21,186$^{(e)}$; 41,322$^{(e)}$</td>
</tr>
<tr>
<td>TEMPamine$^{(b)}$</td>
<td>0.952</td>
<td>21,277$^{(e)}$; 30, 488$^{(e)}$; 41,667</td>
</tr>
<tr>
<td>TEMPone$^{(b)}$</td>
<td>0.778</td>
<td>22,026$^{(e)}$; 42,735$^{(e)}$</td>
</tr>
</tbody>
</table>

(a) 2,2,6,6-tetramethyl-piperidyloxy
(b) (4)-substituted 2,2,6,6-tetramethyl-piperidyloxy
(c) from E. S. Pysh and N. C. Yang, J. Amer. Chem. Soc. 85, 2124 (1963).
(d) from $\lambda_{max}$ of first and subsequent u.v.-visible absorption bands
(e) multiple bands appear from the $n-\pi^*$ and $\pi-\pi^*$ transitions of NO moiety
Table 2. Reduction potentials and excitation energies of the electron acceptor systems being investigated in this study, measured by cyclic voltammetry in acetonitrile referenced to standard calomel electrode (S.C.E.) and by u.v.-visible absorption spectrometry, also in acetonitrile.

<table>
<thead>
<tr>
<th>Acceptor</th>
<th>E_{1/2}^{red} (V)</th>
<th>ΔE/hc (^{(a)}) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzophenone</td>
<td>1.758</td>
<td>28,902; 41,322</td>
</tr>
<tr>
<td>Tetracyanobenzene (TCNB)</td>
<td></td>
<td>38,460</td>
</tr>
<tr>
<td>Tetracyanoethylene (TCNE)</td>
<td>0.0544</td>
<td>37,000</td>
</tr>
<tr>
<td>Tetracyanodiquinodimethine (TCNQ)</td>
<td>0.172</td>
<td>25,640</td>
</tr>
</tbody>
</table>

\(^{(a)}\) from \(\lambda_{max}\) of first and subsequent u.v.-visible absorption bands.
Figure Captions

1. Cyclic voltammogram of diphenylamine in acetonitrile solvent with supporting electrolyte.

2. Cyclic voltammogram of TCNE in acetonitrile solvent with LiClO₄ supporting electrolyte.

3. Plot of aromatic hydrocarbon $E^{ox}_{1/2}$ versus the energy of the charge-transfer band of the hydrocarbon complexes with TCNE.

4. EPR spectrum of the free radicals generated by adsorbing diphenylamine and benzophenone into the supercages of Na-exchanged X-type faujasite zeolite.