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"Photochemical Coal Dissolution"

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The rate of progress on the photoextraction of coal has picked up this quarter but continues to run behind schedule. This is due to unexpected solvent participation in the photochemistry, to work stoppage for fume-hood renovation and to further equipment breakage.

In order to reduce the type of solvent photochemistry reported for pyridine in a previous report, the photochemical reactor was outfitted with a Vycor optical filter. While the difficulties were appreciably reduced, Dewar pyridine formation, hydrolysis and polymerization continue to coat the optical surfaces, unacceptably blocking light passage.

In order to work in a solvent with negligible absorbance of Vycor-transmitted light, experiments were performed in tetrahydrofuran (THF) from which the manufacturer's inhibitor was removed immediately before use. Figure 1 shows the photoproduct yields by weight from 80 min of about 8 ml/min THF flow through our reactor loaded with 200 mg of Pocahontas #3 coal residue. Blanks were also run with no coal. Yields that were greatly in excess of total residue weight were observed when air was not purged from the system. The presence of coal exhibits an inhibiting effect on what clearly must be solvent degradation. The coal inhibiting power on a weight basis is about one-half that of the manufacturer's inhibitor, 2,3-di-tert-butyl para hydroxytoluene (BHT). GC/MS and $^{13}$C, $^1$H NMR analyses of the photoproduct indicate THF ring-opening rearrangements. Similar products were observed from the air-purged experiments. The marked dependence on oxygen concentration suggests peroxide chemistry. However, only minor peroxide product content was indicated and the yields were in at least ten-fold molar excess of the most generous estimates of dissolved or adsorbed oxygen. Thus peroxides, if involved, must be involved catalytically or are recycled, e.g. from decomposition of light-absorbing organic peroxides. It is not clear what species absorbs light in the absence of coal residue.

The differences in THF steady-state photolysis light transmission at 350 nm through the solution exiting the reactor are illustrated in the long-time limits approached in Figure 2. The greater difference in the absence of coal residue is in agreement with the hypothesis that coal is an inhibitor of the THF peroxide formation. As one mode of BHT inhibition is via hydrogen donation, it is plausible that hydrogen donors in the coal residue...
act as comparably powerful inhibitors. Figure 2 also illustrates how the absorbence (calculable from transmittance) time-dependence at any chosen wavelength can be acquired with the computer-interfaced spectrophotometer and with the pump speed controlled via the computer-interfaced solvent pump of the photochemical reactor system.

In order to avoid the suspected peroxide chemistry of THF, the transparent solvent, n-hexane was examined and shown to be photochemically stable in the reactor system. The top trace of Figure 3 shows that the coal residue is not appreciably extracted photochemically in n-hexane, as might be expected from this relatively poor coal extraction solvent.

In order to explore photosensitized coal extraction reactions, an approximately 50% transmittance (@ 350 nm) solution of benzophenone in n-hexane was flowed through the photochemical reactor. The bottom trace of Figure 3 is a blank showing the purely physical silica affinity of benzophenone on the reactor column, due to the transient benzophenone concentration caused by the benzophenone initially adsorbed onto the column of the reactor. When the system was irradiated with coal residue on the column, the third (from top) trace was observed, showing an initial increase in transmittance, followed by a subsequent continuous drop with time. In the absence of coal residue, as shown in the second (from top) trace, the initial increase is observed without the subsequent drop.

NMR indicates that in the absence of coal residue, benzpinacol and 350 nm light-absorbing products of intermediate hexyl radicals are being formed. (It is known that the benzophenone triplet state quenching by hexane is small but not always negligible.) With coal residue on the column, the progressive appearance in solution of more highly colored material suggests that coal residue is competing successfully with solvent for benzophenone attack and is being solubilized.

In summary, a number of successful initial experiments have been performed with the newly constructed, computerized, coal photochemical reactor. The experiments illustrate the care with which solvent sensitizer and irradiation wavelength must be chosen. The experiments, while dealing primarily with undesirable solvent photochemistry, in most
cases demonstrate active participation of coal in the photochemistry. The challenge of the remaining experiments will be to employ what we have learned so far toward maximizing coal photochemistry while eliminating solvent photochemistry.

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Photoproduct Dependence on Pocahontas #3 Coal Residue and Oxygen

Figure 1

Weight Difference Above Thermal (grams)

<table>
<thead>
<tr>
<th>Oxygen</th>
<th>No Residue</th>
<th>0.2 g Residue Present</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purged</td>
<td></td>
<td></td>
</tr>
<tr>
<td>In Air</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Extract Transmission at 350 nm
from Pocahontas #3 Coal Residue.

Flow Rate of 8.8 mL/min
Residue Weight of 0.200 gram

![Graph showing Percent Transmission vs. Time with different symbols representing Blank, Blank & Light, Coal Residue, and Coal Residue & Light.](image-url)