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“Photochemical Coal Dissolution”

David C. Doetschman, Principal Investigator

Department of Chemistry, State University of New York
Binghamton, NY 13902-6016
The remaining types of photochemical extraction experiments originally proposed have now been examined. Experiments in which benzophenone (BP) in solution was employed as a photochemical extraction reagent on pre-extracted coals were performed with Hg arc light through a quartz light filter at a concentration permitting light absorption primarily by the coal. Experiments were done on pre-extracted coals in which tetralin was employed as the photochemical extraction reagent. Finally experiments were performed in which the pre-extracted coal was swelled with BP above its melting point, irradiated through a quartz filter and extracted. The solvent was acetonitrile in all cases.

The BP solution experiments showed more change in transmission (-25 to -35% T) during the coal photoextraction than did previous BP experiments with other optical filters and higher BP concentrations. The general shapes of the traces of %T versus time were similar in shape to those reported in Figure 2 of the September 1995 Quarterly Report. However, the similarity in results for different coals and a similar decrease in transmission in a blank experiment without coal present conclusively point to benzophenone chemistry (no changes with solvent alone). Some fairly universally insoluble, yellow-orange-brown deposits were also present in all BP solution experiments.

Minor transmittance changes in (neat) tetralin coal photoextraction experiments were observed. Like the BP solution experiments, the changes (+7.0 to 7.5%) were similar for the different coals examined and the photochemical blank experiment with no coal present gave a similar increase in transmittance. Tetralin photochemistry was similarly, conclusively implicated. Technical grade tetralin is known to contain naphthalene as the major impurity. Thus we questioned whether the increase in transmittance might have resulted from the photochemical hydrogenation of naphthalene by the predominant tetralin. NMR experiments and standard tetralin purification methods disproved this hypothesis, suggesting that only minor tetralin impurities are being removed by photolysis. The absence of naphthalene photohydrogenation by tetralin was further confirmed in NMR studies of the irradiation of 3:1 W/W tetralin-naphthalene solutions.

The photolysis experiments on the BP-swelled coal residues were designed to maximize BP hydrogen abstraction from the coal residue and to minimize the BP side reactions. The BP: coal residue ratio by weight was 1:1. Conditions in the BP-filled coal pores should maximize the interactions between coal and BP, while minimizing the relative degree of interaction between BP molecules. These BP-swelled coal samples were irradiated through a quartz light filter for 84 min. in the absence of solvent in the photochemical reactor, while suspended on the reactor silica column. The samples were extracted for 84 min. with acetonitrile through the transmittance monitoring system. A trace of one of these runs is compared in Figure 1 with a blank run with a pyrex light filler whose transmitted light does not appreciably excite BP. While there are subtle
decreases in the 350 nm transmittance of the extract over the BP extract in the blank, these do not represent extraction of significant amounts of the coal residue according to yields by weight.

Experiments in the next quarter will turn to the examination of the photochemistry of charge-transfer complexes in coal residues. Larsen and coworkers have observed unusual magnetic behavior in coal-TCNQ and coal TCNE complexes.\(^1\) There is a rich literature of studies of photoexcited paramagnetic states of naphthalene-, anthracene- and phenazine- TCNB charge-transfer compounds.\(^2\)


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401/ BP Coal Doping Experiments

%T @ 350 nm vs. Time, irrad. 84 min, then extract 84 min.

Figure 2.

- pyrex expt.
- quartz expt.