HYDROGEN TRANSFER PROPERTIES OF SOME COAL PROCESS RECYCLE SOLVENTS (1)

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INTRODUCTION

We are interested in the chemical properties of direct coal liquefaction recycle solvents. Of immediate concern is the chemistry during the liquefaction step which results in the "hydrogen shuttling" or "hydrogen transfer" reaction. The question of which components of solvent mixtures make a significant contribution to "hydrogen shuttling" or "hydrogen transfer" during the conversion process has received modest attention.(2,3,4) It appears that this problem has been addressed from the viewpoint of experiments with individual model compounds using them as solvents or, alternatively, with synthetic mixtures composed of two to six compounds. In those intentionally simplified solvent systems, reactions of the components under liquefaction conditions can be followed with varying degrees of convenience. The situation is different with authentic recycle solvents. The desire to gain insight into the reactions of components of these materials under liquefaction conditions offers exceptional opportunities not describable in terms of convenience, see Fig. 1 for example. Nevertheless, because of our interest in the mechanism of hydrogen transfer, we have undertaken an investigation of hydrogen exchange in the recycle solvents.

Our approach to the subject makes use of the observation of the hydrogen-deuterium exchange reaction. The problem is conceived to be threefold as follows: first, we have determined the relative degree of hydrogen-deuterium exchange of selected individual pure compounds which are thought to be present in recycle solvents; second, we have determined the composition (primarily the major components) of several recycle solvents; and third, for one recycle solvent, we determined which compounds undergo hydrogen-deuterium exchange when heated at coal conversion temperatures in three separate experiments with three different deuterium sources.

EXPERIMENTAL

Individual pure compounds. In a typical experiment the compound in question was heated with an amount of diphenylmethane-d_2, Ph_2CD_2, such that the number of deuteriums was equivalent to the number of hydrogens in the investigated compound. The reactions were carried out in a 7.5 ml stainless steel tubing bomb at 400°C for the appropriate amount of time. The bomb was usually charged with about 2 g of reactants. Workup procedures varied depending on the properties of the mixture. In each case gc analyses were obtained to determine the number of products present. When possible, diphenylmethane-d_2 was recovered and distilled in vacuum and the compound under investigation was either crystallized or sublimed. The samples were then analyzed by ^1H nmr, ^2H nmr, and gc-ms. Exchange was calculated from these data and the results are recorded in Table 1.

Recycle solvents. These materials were obtained from the Wilsonville pilot plant and from Gulf Research and Development Company.(5) Gc analyses were obtained using a Hewlett-Packard 5880 gas chromatograph fitted with a 15-meter glass capillary column coated with OV-101, and a flame ionization detector. Gc-ms data were obtained using a Hewlett-Packard 5995A gas chromatograph/mass spectrometer fitted with the same column. Exchange experiments were done using three different

deuterium sources, diphenylmethane-d_2, pyrene-d_n, and D_2 gas. The solvent chosen for these experiments was a Wilsonville V-131, Hydro Run 257.12-8, to which had been added light SRC, subsequently referred to as "hydrosolvent." To a 3-ml stainless steel tubing bomb, there was added 1 g of hydrosolvent followed by 1 g of diphenylmethane-d_2. The bomb was closed and heated in a fluidized sand bath for two hours. The contents of the bomb were then removed, a portion was dissolved in acetone for analysis by gc and gc-ms. In a second experiment, pyrene containing 56.5% deuterium was used. The third experiment was done in a 7 ml tubing bomb containing 1 g of hydrosolvent under 540 psi deuterium gas pressure. A control experiment in which hydrosolvent alone was heated showed that no significant compositional changes took place due to the severe reaction conditions as indicated by capillary gc analysis, Figure 1, and nmr spectroscopy, Figure 2. Further information on other recycle solvents will be given in a subsequent publication.

DISCUSSION AND RESULTS

Several groups have used deuterium tracer techniques to investigate hydrogen transfer to coal during liquefaction.(6,7,8,9) Generally, these experiments make use of deuterium containing model solvents to produce coal-derived products which were carefully monitored for deuterium content and distribution. The alternative approach, that is, the use of a deuterium exchange source followed by monitoring deuterium content and distribution in coal-derived solvents is dealt with here. The choice of compounds to be used for deuterium sources is based on earlier work.(10). We showed that the activation energy for exchange of deuterium in the CD_2 group of diphenylmethane-d_2, when heated with ordinary tetralin, is 134 kJ/mole. This value is compared with the activation energy of 171 kJ/mole for exchange of the $-CD_2-CD_2-$ deuteriums of bibenzyl-d_4, and with approximately 256 kJ/mole for thermal cleavage of the central C-C bond of bibenzyl.(11) Therefore diphenylmethane provides a good source for easily exchangeable deuterium.

The choice of deuterated pyrene as another D-exchange source is derived from reports in the literature (3,4) that pyrene is a good nondonor solvent for coal conversion and that it acts as a hydrogen carrier. The third deuterium source, D_2 gas, was used partly because most coal conversion processes are accomplished under high hydrogen gas pressures. Consequently we are curious about the extent of reactivity of hydrogen gas with relation to how it is carried to coal by solvent.

The solvents associated with SRC processes are usually discussed in terms of their H-donor content as exemplified by hydroaromatic compounds. These compounds may be produced by partial hydrogenation of some part of the coal-derived product. By contrast, short contact time (SCT) solvents may need to function especially as H-transfer agents rather than H-donors. Key molecules for this purpose are believed to be the polynuclear condensed aromatic compounds. Considering this viewpoint, which may be somewhat oversimplified, we decided to study a group of aromatic compounds, including polynuclear aromatics, for their ability to undergo hydrogen exchange reactions, it being assumed that reactivity toward hydrogen exchange is related to hydrogen shuttling.

The procedure for accomplishing exchange of the aromatic hydrogens is given in the experimental part and the data are recorded in Table 1. Three aspects of the data are immediately recognized: 1) exchange rate is related to structure as in comparing anthracene and phenanthrene; 2) exchange rate is related to stability as exemplified by naphthacene and 9-phenanthrol; and 3) exchange appears to be positionally selective in molecules such as phenanthidine, beta-naphthol, and methylnaphthalene.

In general, polynuclear aromatic hydrocarbons undergo hydrogen-deuterium exchange slowly. The results with pyrene are of particular interest in view of

the reports that pyrene is an efficient solvent for coal conversion. The implication is that pyrene functions as a good hydrogen transfer agent. The reaction pathways are not known in detail; however, hydrogen exchange through hydrogenation-dehydrogenation may well be involved. In our study, pyrene underwent exchange very slowly, only 1.2% in 2 hours. We then observed that extensive exchange takes place, 30.7% in 2 hours, when pyrene and diphenylmethane are heated together in the presence of naphthacene, a compound which itself undergoes extensive decomposition and exchange under the experimental conditions. Because of this observation, we were curious to know if a pyrene-diphenylmethane-d_2 mixture would undergo rapid exchange when heated in the presence of a third compound which exchanges rapidly but is otherwise stable. The candidate for this experiment was phenol. Phenol itself undergoes exchange. When phenol, pyrene, and diphenylmethane-d_2 were heated for two hours, the phenol was 14% exchanged but the pyrene was only 0.84 percent exchanged. In another experiment, pyrene heated with bibenzyl-d_4 for 2 hours at 400°C undergoes 2.9% exchange. The reisolated reaction mixture also contained small amounts of dihydropyrene and a more saturated pyrene. Bibenzyl slowly undergoes homolytic bond cleavage at a known rate (11) under these conditions to produce free radical intermediates. From the information above it is tempting to propose that pyrene functions as a hydrogen shuttling agent through radical intermediates but other mechanisms could be involved.

It is impossible, in the space provided, to give all the exchange data available for molecules present in recycle solvents. The particular solvent we studied contained methylnaphthalene, biphenyl, and diphenyl ether as the most abundant components. Of these three components, only methylnaphthalene underwent H-D exchange. This result was observed with all three deuterium sources.

More than 200 compounds were identified in the hydrosolvent. In addition, there were numerous components present in minor amounts which could not be reliably characterized because of ms background interference. The solvent contained very small quantities of the important components, tetralin, and pyrene, less than 0.5%. Although similarly small quantities of isomers of methyl pyrene were present, the three and four condensed ring polynuclear aromatic compounds were disappointingly scarce. The most abundant series of compounds present were mono- and polymethylnaphthalenes and long straight chain saturated hydrocarbons.

The exchange data for the recycle solvent are summarized as follows:

1. Aliphatic hydrocarbons did not exchange. Aromatic hydrocarbons like naphthalene, biphenyl, diphenyl ether, and phenanthrene show little observable exchange with all three deuterated reagents, although phenanthrene did undergo exchange to about 1% when pyrene-d_n was used.

2. Certain compounds underwent extensive exchange with all three deuterated reagents. These compounds were substituted aromatics; methyl- and polymethyltetralins, methyl- and polymethylindanes, methyl- and polymethylnaphthalenes, fluorene, the methyl substituted pyrenes and dihydropyrenes, methyl- and dimethylbiphenyl, and phenols.

3. The pyrene present in the solvent exchanges extensively with D_2 gas but only slightly with diphenylmethane-d_2.

4. The exact relative degree of exchange in the three experiments can be calculated for only a limited number of compounds because of gc-ms resolution problems.

5. There was one surprise. In all three experiments toluene showed extensive exchange. This result is unexpected because earlier experiments in this laboratory suggest that toluene should be reluctant to undergo exchange.

We conclude from the above experimental evidence that the methyl substituted aromatic and hydroaromatic compounds in the recycle solvent make the most important contribution to hydrogen shuttling and hydrogen transfer.

Table 1. Degree of Hydrogen-Deuterium Exchange (%) of Selected Aromatic Compounds with Diphenylmethane-d_2 at 400°C

Compound	2 hr	5 hr
Benzene	0	0
Naphthalene	1.8	-
Diphenylmethane	0	Trace
Aromatic Hydrogens		
Phenol	15	-
Acenaphthene	Unstable at 400°C	
Acenaphthalene	Unstable at 400°C	
Biphenyl	-	0
Diphenylether	-	0.4
1,2-Benzanthracene	3.92	13.9
Naphthacene	38.9	
	Decomposes	
Chrysene	0.93	2.20
Perylene	6.8	15.0
Triphenylene	2.02	3.2
Phenanthrene	0.12	1.56
Anthracene	10.06	16.91
Pyrene	1.20	5.40
Hexahydropyrene	6.03	18
β-Naphthol	9.0	12.8
9-Phenanthrol	21.1	22.75
	Decomposes	
β-Methylnaphthalene	5.34	7.73
Dibenzofuran	trace	trace
Dibenzothiophene	trace	trace
Carbazole	6.11	19.84
Phenanthridine	6.69	8.97

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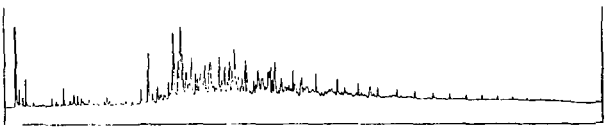

Figure 1. Capillary gc trace of the coal process recycle solvent, "Hydrosolvent." The most intense peak is diphenyl ether.

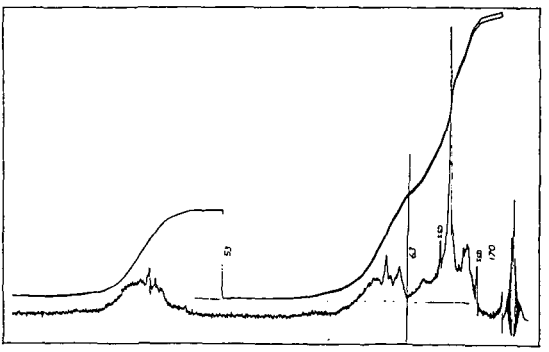

Figure 2. 60 MHz ^{1}H nmr spectrum of the coal process recycle solvent, "Hydrosolvent."