

PHYSICAL ORGANIC CHEMISTRY OF COAL LIQUEFACTION

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The direct conversion of coal to liquid fuels is a complex chemical and physical process. The challenge of developing an understanding of the molecular details of this process has provided physical organic chemists great opportunities to ply their trade. Although dramatic breakthroughs may be lacking, progress has been made bit-by-bit. Along the way, a fascinating chemistry has been revealed. The extreme reaction conditions required for effective liquefaction have added an extra degree of interest to the development of this field.

Direct liquefaction is most often practiced by the addition of hydrogen to coal in some manner. The hydrogen content of the products is thus greater than that of the feedstocks. Accordingly, one of the central interests of our effort over the years has been the chemistry of hydrogen transfer reactions. Some form of hydrogen transfer is involved in nearly every chemical mechanism of importance to liquefaction (1). To fully understand the hydrogen transfer chemistry is to understand a large portion of the whole of liquefaction chemistry.

Many basic types of hydrogen transfer reactions may take place under liquefaction conditions. In the face of this inherently complex system, numerous experimental techniques for deriving information about these reactions have been developed. Some approaches have aimed at obtaining fundamental information about individual reactions, often by use of pure compounds under liquefaction conditions. Other approaches have focused on tracking the transfer reactions in liquefaction systems containing coal, with interest in finding what functional groups are the major players. Still another approach is a hybrid, using the addition of individual compounds to coal liquefaction feed slurries to gain information on the reaction environment under actual liquefaction conditions.

Past work in this laboratory on hydrogen transfer chemistry focused on the rates of transfer from individual compounds thought to be representative of constituents of liquefaction solvents to a simple, resonance-stabilized free radical (2,3). For this purpose, the benzyl radical was chosen as the hydrogen acceptor because it represents, in general, the type and activity of radicals that are expected to form in coal under thermolytic conditions. One of the earliest mechanistic interpretations of liquefaction, in terms of simple molecular reaction steps, postulated that thermal scission of the weaker bonds in coal produced free radicals. The capping of these reactive intermediates by hydrogen transfer from hydroaromatic

compounds in the solvent before they could recombine led to liquid products (4). Although this simple, early view has since been shown to be incomplete, it nonetheless accounted for several important observations such as the correlation of the degree of coal conversion with the degree of conversion of hydroaromatic compounds in the liquefaction solvent to aromatic compounds. It also contained the important concept that the distribution of liquefaction products between extractable materials and residues results from the outcome of competitive reactions. Thus, the relative rates of hydrogen transfer versus the rates for condensation reactions are of importance because they relate directly to product distribution and product quality. If the rates of transfer from different hydrogen donors vary according to their structure, then it is of value to know the relative rate constants for transfer as well as the total concentration of donable hydrogen.

A series of competition experiments was performed to establish a scale of relative hydrogen transfer rate constants (2,3). The benzyl radical was provided by the thermolysis of easily decomposed compounds, dibenzylmercury (3) or dibenzyl diazene (2), at modest temperatures, typically 170°C. Competition for the radicals was established between triphenylsilane-D and one of a number of donors, such as tetralin or dihydroanthracene. The relative rate constants were derived from the amount of deuterium incorporated into toluene, the product derived from the transfer of hydrogen or deuterium to a benzyl radical. These data illustrate that the rate constants vary considerably. For example, the value for transfer from dihydroanthracene is about a factor of 30 greater than that from tetralin. In perspective, such relative values bear on several aspects of liquefaction mechanisms. First, in regard to liquefaction yields, the type of donable hydrogen is important, not just the total amount of donable hydrogen. Second, the predominant free radicals generated in the liquefaction system should result from abstraction of hydrogen from the sites of greatest relative reactivity. The structures to be exhausted first among the different donors of a complex mixture may then be predicted. Also, the hydroaromatic radical species resulting from competitive abstraction reactions may be anticipated. The nature of these radicals takes on importance in light of the recent work showing that hydroaromatic radicals may serve to induce cleavage of strong bonds by donation of hydrogen atoms (5). As shown in the reference, hydrogen transfer from 9-hydroanthracenyl radical to an alkylaromatic compound yields anthracene and the cleavage products, which are the corresponding aromatic compound and the alkyl radical derived from the alkylaromatic. Finally, although the relative rate constant for hydrogen abstraction from each of the various donors is an important factor, it should be noted that this one parameter is hardly an infallible guide to success in liquefaction. It is only one part of the complicated mechanism, and simple attempts to correlate liquefaction yields with just one parameter most often fail.

A sidelight to these investigations arose from the observations that the kinetic deuterium isotope effects for transfer were unexpectedly large (6). A value for k_H/k_D as large as 13.0 was observed at 110°C for the transfer from tetralin to benzyl radical.

Detailed investigations of this curiously large effect led to the conclusion that a tunneling mechanism must come into play for hydrogen transfer between these benzylic reaction partners (6). This provides another fascinating example of the complexity of the chemistry that takes place during liquefaction.

The second means to investigate hydrogen transfer reactions uses quite a different approach. In this approach, the important thing is the amount of hydrogen used or produced in various general types of organic reactions during liquefaction. For the purposes of discussion and accounting, the utilization of hydrogen may be broken down into four general types of reaction: production of light hydrocarbon gases; removal of heteroatoms by formation of water, H₂S, or ammonia; reduction of aromatic carbon; and the breaking of bonds, either those in the coal matrix or those in the liquefaction solvent (7). The amount of hydrogen used in each of these general processes may be determined by a combination of elemental analyses, mass balance data, and NMR determinations of aromaticities. The appropriate differences are then taken between the values for the starting materials and the values for the total organic products, including gases, methylene chloride extracts, and the extraction residue. From the results, some important general trends emerge. The aromaticity of the products tends to increase with liquefaction temperature. An overall gain in aromatic carbon was observed when temperatures over 400°C were reached (7). This trend was found even at 2000 psig hydrogen whether or not a catalyst was present (8). Thus, the higher temperatures normally used in the common liquefaction processes tend to work against the goal of coal hydrogenation.

Study of the effect of molybdenum catalysts used under low severity conditions also led to interesting observations. From the differing patterns of hydrogen utilization in catalytic and non-catalytic systems, one function of a dispersed catalyst derived from ammonium molybdate was to lessen the net number of retrogressive or condensation reactions (8). Thus, in comparing liquefaction experiments at 450°C, the number of hydrogens used per 100 carbon atoms for matrix bond breaking increased on addition of catalyst, but the number released from dehydrogenation of aromatic carbons was nearly the same. By following these changes as a function of reaction time, a picture of the sequence of utilization patterns could be developed (9). The results of this work indicated that condensation reactions were prominent during the first 10 minutes of reaction, after which cleavage reactions began to predominate. On the other hand, conversion to THF soluble material increased steadily throughout this same period of time. Obviously, a one-to-one correspondence of net bond cleavage and conversion does not exist. This work reveals that liquefaction kinetics appear differently according to whether conversion or hydrogen utilization is taken under study.

The critical nature of the first few minutes of a liquefaction reaction has recently become evident again through observations of the changes in total pressure within the liquefaction reactor with time. The total pressure was monitored during the course of the liquefaction reaction by mounting pressure transducers on microautoclaves. The data in Figure 1 for an Illinois No. 6 coal

show that the change in total pressure in the reactor is a function of the amount of ammonium tetrathiomolybdate added. The thiomolybdate serves as a precursor that is reduced in situ to form a molybdenum sulfide catalyst. If no catalyst precursor is added at all (data not shown), the increase in total pressure during the first 10 to 20 minutes of reaction is even more prominent than for the smallest addition of catalyst. At still larger additions, the pressure increase is not observed at all. Gas analysis of the products indicates that the major species in the gas phase after hydrogen is CO_2 . The amount of CO_2 formed is not much different whether or not catalyst is present. Thus, it appears that at the higher concentrations, the catalyst acts in some way to induce the transfer of gas phase hydrogen in an amount that nearly balances the CO_2 evolved during the initial liquefaction. At the comparatively low temperature used for liquefaction here, it was also possible to see an increase in the conversion of coal to THF soluble material as a consequence of catalyst addition. Separate techniques thus point to the early time period of the liquefaction reaction as being especially critical to the pattern of hydrogen utilization. Clearly, any particular pattern is not universal, because many variables govern the kinetics of the four basic types of reaction. However, the hydrogen utilization methodology provides a means to monitor net changes in the patterns of the hydrogen transfer reactions as the process parameters are manipulated.

A third general methodology employed in our laboratories has been the use of probe molecules to "report" on conditions in the hydrogenation reactor (10,11). Probe molecules serve the general function of sensing the reaction environment throughout the course of the liquefaction experiment. The information gained relates to the way the reaction environment is changed by the addition of components normally used in liquefaction such as coal, catalysts, and liquefaction solvents, or to changes in the process variables such as temperature, reaction time, or hydrogen pressure. Thus, the intent is not to ferret out the reaction mechanisms that are responsible for liquefaction, but to determine if a particular process variable selected for study may cause changes in the rates of certain types of reactions. Thus, a relatively stable compound, cis-decalin, was used to monitor the relative rates of free radical reactions as coal was added to the reaction system (11). It was shown that the presence of free radicals accelerates the isomerization of cis- to trans-decalin. The rate of approach to the equilibrium value for the ratio of cis- to trans-decalin was then used to evaluate the activity of the radicals generated in the liquefaction reactor. The addition of coal accelerated the rate of approach to equilibrium, thus indicating that coal acts as a free-radical reaction initiator. Further, the rate of approach to the equilibrium ratio conformed reasonably well to pseudo-first order rate behavior in the presence of coal, indicating that the activity of free radicals remained constant over the course of the reaction which lasted in this case up to three hours.

Other probes serve other purposes. For example, 1,3-dimethylnaphthalene, as described in the accompanying (12) and a prior paper (11), has been used to probe dealkylation reactivity. This probe revealed that the addition of coal increased the yield of

dealkylated products, indicating that coal may initiate hydrogen atom transfer reactions resulting in alkyl-aromatic bond cleavage, especially under hydrogen gas pressure. Cleavage of such bonds results from the transfer of hydrogen atoms from a donor or by the attachment of a free hydrogen atom. Each source of hydrogen has a different selectivity for attack at the 1- versus the 2-position on naphthalene. Significantly, the preference for cracking at the 1-position increases with addition of coal. Transfer of hydrogen atoms from hydroaromatic free radicals is known to be more selective for the 1-position than attack of the free hydrogen atom itself (5). Thus, the increase in selectivity indicates that a portion of the cracking reactions result from hydrogen atom transfer from active donors of the coal or coal-derived materials rather than the free hydrogen atom. This portion of the cracking reactions takes place primarily as a result of the direct interaction of the probe with added coal, and thus reflects the reactivity of the coal-derived hydrogen transfer agents.

Another approach to the problem of hydrogen transfer chemistry has been recently taken up. The coal-hydrogen-catalyst interaction is of fundamental importance to liquefaction schemes, and particularly those that focus on low severity processing conditions. In this connection, one of the major puzzles of liquefaction chemistry is how hydrogen transfer takes place between a solid, heterogeneous catalyst and a solid or nearly solid substrate like coal. A pulse-flow microreactor was constructed and demonstrated to be a useful means to study this chemistry (13). As shown in Figure 2, the reactor is a simple device designed to allow a sample to be heated in a tube placed in a clam-shell furnace. A stream of argon is passed through the tube and sampled by a quadrupole mass spectrometer that is capable of monitoring up to five different masses at once. An injection loop allows the introduction of a pulse of deuterium gas upstream of the heated sample. Using this apparatus, a series of samples was heated in separate experiments to determine if useful information could be obtained regarding the interaction of a solid, dispersed catalyst with coal in the absence of any liquefaction solvent. The first experiment indicates that some exchange takes place when a coal is heated by itself. As shown in Figure 3, passage of deuterium over coal heated to 425°C results in the formation of small peaks for HD and H₂. The major peak due to D₂ itself remains. Thus, deuterium does exchange with hydrogen on coal in the absence of added catalyst. The next experiment involved heating MoS₃ by itself. This material has been used as a catalyst precursor by others at our laboratory with good results (14). As shown in Figure 4, when MoS₃ is heated to 400°C, the pulse of deuterium results in a family of pulses at m/e of 32, 33, and 34. A peak at 36 is also associated with this trio, but not shown in this figure. This family of peaks is due to D₂S and H₂S and their ionic fragments, and indicates that, under reducing conditions, hydrogen sulfide is evolved from the catalyst. Presumably, the hydrogen contained in the sulfides detected has come from exchange between water and D₂S at some point downstream from the catalyst bed. Significantly, no HD or H₂ is observed. Under these conditions, the catalyst is probably not yet fully reduced, and the evolution of hydrogen sulfide may reflect

continuation of the transition from MoS₃ to MoS₂. Post-run characterization of the recovered catalyst may determine the final form of the material reached by the conclusion of the experiment.

The third experiment combined coal and catalyst. A mixture of the MoS₃ catalyst precursor and a Pittsburgh No. 8 coal from the Argonne Coal Sample Bank was heated, and its behavior was found to be much different than either material alone. (By itself, the Pittsburgh No. 8 coal responded very much like the Illinois No. 6 coal used in the initial experiment.) At 375°C, the pulse of deuterium was not detected, implying that it was taken up by the coal/catalyst mixture. This behavior was not seen when either coal or this catalyst was used separately. At a higher temperature (Figure 5) the deuterium pulse is still missing, but a pulse of H₂ with roughly the same magnitude appeared. After cooling to room temperature, the sample was put through the same heating cycle once more. This time, hydrogen-deuterium exchange reactions were noted when the temperature reached 225°C, far below that required on initial heat-up. This may reasonably be interpreted on the basis that the catalyst precursor, once activated by heating at a higher temperature, may now show activity at a much lower temperature. Again, the pulse of deuterium, when admitted at temperatures above 250°C, was completely removed and a pulse of H₂ in the same shape appeared in its place. At present, the mechanism for this exchange process is not understood. However, it points out in a dramatic fashion that a "dry" system does exhibit chemical communication between coal and dispersed catalyst. These experiments are still in their infancy. The positive results in hand provide good reason to suspect that more can be learned about this fascinating transfer of hydrogen between coal, catalyst, and gas-phase hydrogen.

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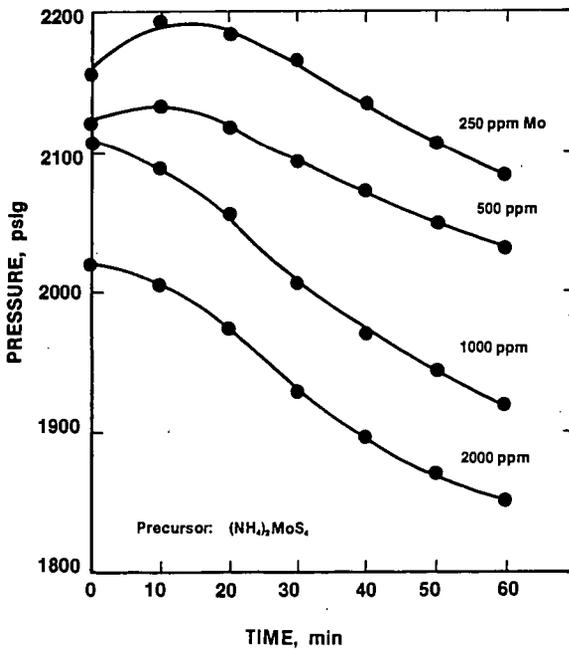


FIGURE 1. TOTAL PRESSURE VERSUS TIME FOR LIQUEFACTION OF ILLINOIS No. 6 COAL AT 350°C.

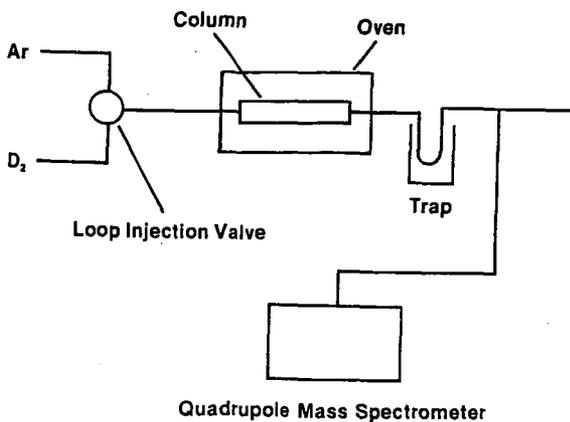


FIGURE 2. PULSE-FLOW MICROREACTOR FOR MONITORING DEUTERIUM EXCHANGE.

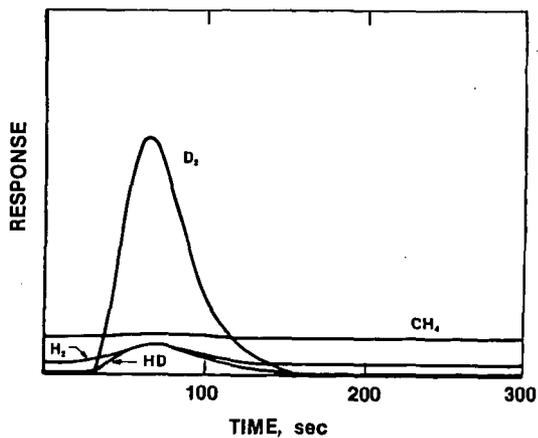


FIGURE 3. EXCHANGE EXPERIMENT WITH DEUTERIUM PULSE AND ILLINOIS No.6 COAL HEATED AT 400°C.

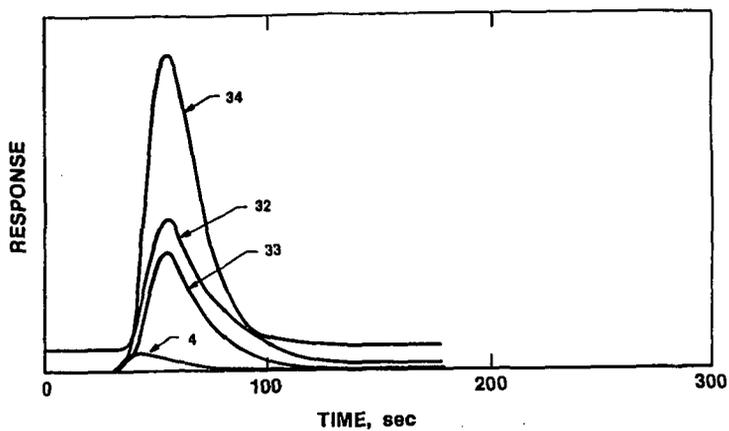


FIGURE 4. RESPONSE FROM DEUTERIUM PULSE AFTER MoS_3 WAS HEATED TO 400°C .

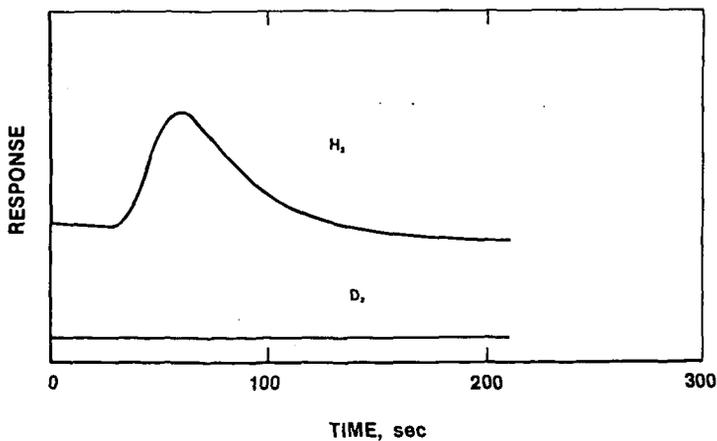


FIGURE 5. RESPONSE FROM DEUTERIUM PULSE AFTER A MIXTURE OF PITTSBURGH No. 8 COAL (1.9 g) AND MoS_3 (0.1 g) WAS HEATED TO 425°C .