

THE CHEMICAL ORIGIN OF SYNERGY IN LIQUEFACTION AND COPROCESSING

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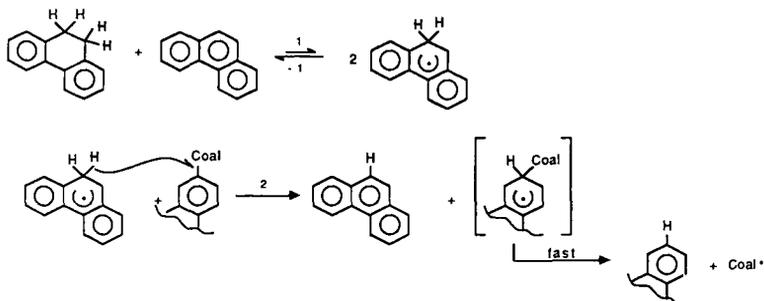
INTRODUCTION

The question of possible synergistic effects for coal liquefaction has been raised recently in the context of coprocessing and also in that of straight donor-solvent liquefaction. Synergy is generally defined to occur when the effect of a combination of components exceeds the sum of the effects of the individual components. The existence of such synergism is more difficult to demonstrate in the coprocessing context, because liquefaction of coal alone, that is, in the absence of any other component (e.g., residual oil), is not viable in process terms, and therefore one of the boundary conditions is not available. Synergism can be much more readily assessed in the context of straight liquefaction, where there is always a liquefaction medium, which can be made up of a number of components. This paper specifically addresses liquefaction data, but the conclusions drawn are all equally applicable to coprocessing.

Recently there have been several reports of coal liquefaction illustrating the interactive effect of various components (1-3). We have used these results in conjunction with an improved mechanistic model for coal liquefaction to help shed some light on the chemical origin of such interactive effects. First, it should be noted that the traditional liquefaction mechanism, which ties liquefaction effectiveness to the efficiency with which donor components scavenge fragment radicals formed in the spontaneous thermal scission of the coal structure, cannot easily accommodate interactive effects. On the other hand, such effects would actually be anticipated for mechanisms that are not unimolecular in solvent components, but, in general terms, involve reaction of one component with another to form an intermediate, which then reacts with the coal component. Specifically, we show that the various H-transfer processes that we have hypothesized as leading to bond cleavage by "solvent-mediated hydrogenolysis" clearly fall in the second category of reaction type. As previously discussed by us (4,5), most of these processes require both a hydrogen "donor" species* and an "acceptor" species in order to form the active H-transfer intermediate,

*In the discussion that follows, we use the word "donor" specifically to mean a hydrocarbon, whether aliphatic, alkyl-aromatic, or hydroaromatic, that can contribute a hydrogen atom to a radical or other acceptor. We make this distinction because some of these substances, such as fluorene, are good hydrogen-atom donors in this sense but are not good donor solvents.

a cyclohexadienyl "carrier" radical, which can transfer hydrogen to engender cleavage of even strong bonds.



In the following paragraphs, we summarize two of the more recent and more striking examples of synergism. One of these uses only nonhydroaromatic donors and the other hydroaromatic donors. We then discuss, in qualitative terms, how a coal-liquefaction picture that includes strong bond hydrogenolysis mediated by solvent carrier radicals can easily accommodate the liquefaction results. The case involving hydroaromatic solvents is more amenable to mechanistic modeling, and for this case we will compare cleavage rates predicted by the model with the actual liquefaction results. Finally, we extend the mechanistic insight gained in rationalizing the positive interaction among solvent components in coal liquefaction to account for the interactive effects reported for coprocessing.

EXAMPLES OF REPORTED SYNERGY

1. Improvement of Hydroaromatic Solvents by Addition of Non-Donor Aromatic Components

Cassidy and coworkers have very recently published results using a hot-charged, time-sampled autoclave that show substantial increases in oil yield resulting from the replacement of half of the tetralin in the solvent with various aromatics (1). Figure 1 shows the oil yields as a function of time that were obtained when three different PCAH were added to the solvent. Pyrene is clearly the most effective additive, increasing the oil yields by some 30 percentage points at very short as well as longer reaction times. Anthracene and phenanthrene are somewhat less effective, in that order. These changes are remarkable, particularly since the PCAH replaced half of the tetralin, such that the donor content was actually lowered from 50 to 25%! The authors recognized this and evidently took particular pains to assure themselves that the results were reproducible.

These results are parallel to, but more striking than, earlier results of Derbyshire et al., who reported that conversion of an Illinois No. 6 coal

(to THF-solubles) in 70% pyrene, 30% tetralin was better than conversion in pure tetralin, at two different hydrogen pressures (2).

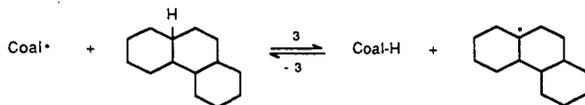
2. Aromatic Components Make Accessible Pathways for Bond Cleavage via Solvent-Mediated Hydrogenolysis

The results of Clarke et al. provide a dramatic illustration of the importance of H-acceptor solvent components (3). These workers report that whereas conversion (to quinoline-solubles) of an 84% carbon coal in various perhydro-PCAH was quite poor, it improved slightly when naphthalene was added, and improved quite markedly when PCAH such as phenanthrene or pyrene were added. These results are depicted in Figure 2. The conversion levels achieved with the 3- or 4-ring PCAH (good acceptors) are almost as high as that achieved with octahydrophenanthrene, which is known to be an excellent solvent. The authors also note that only in the presence of the 3- or 4-ring PCAH is there any significant dehydrogenation of the perhydroaromatics. However, in the absence of the PCAH, the perhydroaromatics were observed to undergo cis-trans isomerization, indicating the formation of bridgehead radicals.

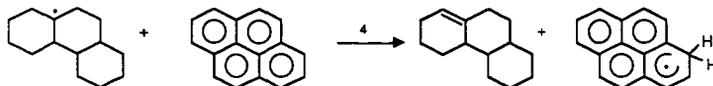
RATIONALIZATION IN TERMS OF SOLVENT-MEDIATED HYDROGENOLYSIS

The above results are entirely consistent with (and so far as we know cannot be rationalized without) the mechanistic picture of coal liquefaction that includes solvent-mediated hydrogenolysis of strong bonds by radical hydrogen-transfer (RHT): formation of H-atom "carrier" species from PCAH, followed by H-transfer from these carrier species to ipso- positions on aromatic clusters within the coal structure that bear linkages to other clusters, resulting in hydrogenolysis of these linkages.

Any thermally produced coal radicals can, at a modest rate, abstract aliphatic hydrogens from perhydrophenanthrene or other perhydroaromatics.



In the absence of any PCAH molecules, which can act as H-acceptors, the cycloalkyl radicals will recapture a hydrogen (reaction -3) or undergo a β -scission of a C-C bond to produce an olefin and another alkyl radical. β -Scission of a C-H bond leading to free H-atoms, which could engage in further bond cleavages, is estimated to be about 6 orders of magnitude too slow to compete effectively with either of these reactions (6-8). On the other hand, transfer of a hydrogen to a PCAH molecule from the cycloalkyl radicals is comparable to the hydrogen recapture (reaction -3) or the β -scission of a C-C bond.



Transfer of a hydrogen to a PCAH molecule produces a cyclic olefin and a cyclohexadienyl radical. These cyclohexadienyl radicals can result in hydrogenolysis of other bonds in the coal structure by RHT (reaction 2). Furthermore, the cyclic olefin has much weakened allylic C-H bonds and the removal of one of these hydrogens ultimately leads to the formation of hydroaromatic structures. Thus, the PCAH molecules can channel the hydrogens available in the perhydroaromatic molecules into useful cleavage reactions.

The above scenario has been borne out more rigorously with the help of a mechanistic numerical model for the case of Cassidy et al. For modeling purposes, we used the cleavage of dinaphthylmethane as a surrogate for those structures in coal that cannot cleave by simple thermolysis under the conditions of reaction, and whose cleavage has to be mediated by the solvent. We modeled the cleavage of dinaphthylmethane with the donor hydroaromatics alone and for cases in which a portion of the hydroaromatic replaced by a non-donor species such as pyrene or anthracene.

Figure 3 shows the computed rates of cleavage resulting from H-transfer (to the ipso position of a naphthalene-X structure) by RHT and free H-additions, as well as the total cleavage rate for a 10:1 dihydrophenanthrene:phenanthrene mixture. Also shown (dark bars) are the rates computed for the case where 10% of the dihydrophenanthrene has been replaced by anthracene. The replacement results in a contribution from a step labeled RHT', that is, H-transfer from the anthracene-derived carrier radical. It also results in a substantial increase in the concentration of, and therefore transfer from, the hydroanthryl radical, and in an increase in the free H-atom contribution, such that the overall increase in cleavage rate is 120%. Examination of the various reactions producing and consuming the hydrophenanthryl radical shows that the increase is mainly due to the rapid formation of AnH', owing to the very good H-acceptor nature of anthracene. The increased AnH' concentration then results in an increased production of PhenH' through reaction of AnH' with PhenH₂. The increase in computed cleavage rate is larger or smaller as the system is poorer or richer, respectively, in "native" acceptor (e.g., phenanthrene). In other words, systems that are "over-hydrogenated," or poorest in acceptors, appear to benefit most from the addition of a good acceptor.

The increased production of PhenH' is in part analogous to the reduction of anthracene by dihydrophenanthrene, which was reported by Billmers and Stein to be catalyzed by the addition of small amounts of dihydroanthracene (9). In both cases a large pool of AnH' radicals produces additional PhenH' by abstraction of H from PhenH₂. In the case described by Stein, this pool of AnH' radicals arises because of the very good H-donor quality of the added AnH₂. In the present case, the radical pool increases because of the very good acceptor quality of anthracene itself.

KEY HYDROGEN-TRANSFER REACTIONS IN COPROCESSING

In coprocessing of coals and heavy oils, we have a situation where the heavy oils have a relatively large amount of aliphatic hydrogen that is potentially useful for cleavage of coal structures. We suggest that the PCAH in the coal interact with the aliphatic hydrocarbons in a way very similar to the one we have described the case of coal conversion results in PCAH and perhydro-PCAH reported by Clarke et al. (3), making it possible to utilize the hydrogen from aliphatic compounds. In addition, because petroleum resids contain some amount of polycyclic aromatics (typically as long-chain alkyl aromatics), the benzylic hydrogens on their side chains provide a source of relatively weakly bonded hydrogens that can, along with the coal radicals, serve as initiating sources. Similarly, to the extent that the β -scission breakup of the alkyl chains produces some amount of olefins (even in the presence of H_2), the allylic hydrogens on these olefins will be easily transferred. These aspects of coprocessing chemistry are currently being explored by Bockrath and coworkers using pure hydrocarbons as models for the resids (10). The results of their studies can be expected to provide tests for some of the speculations made here.

SUMMARY

Analysis of synergistic effects of solvent components in coal liquefaction studies indicates that the key chemical features of coprocessing component interaction are:

- (1) Coal radicals generate aliphatic radicals from the resid;
- (2) The aliphatic radicals can undergo β -scission of C-C bonds to convert the resid, or can transfer a hydrogen to the PCAH to form carrier species capable of engendering hydrogenolysis;
- (3) In the presence of gaseous hydrogen, radical abstraction from H_2 adds a propagation step that facilitates the utilization of H_2 for hydrogenolysis.

These reactions allow the hydrogen in the aliphatic resid components, which are known to be poor liquefaction solvent components, to be made available for coal conversion.

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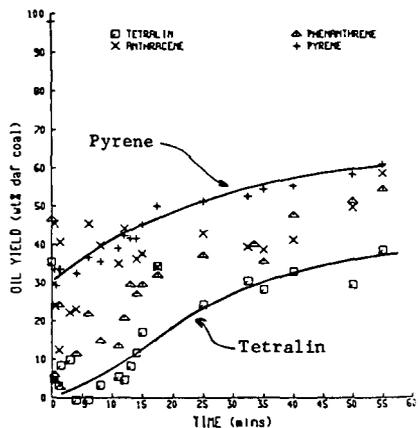


Figure 1: Impact of PCAH addition on liquefaction of Illinois No. 6 coal in tetralin. (Figure from Cassidy et al., Ref. 1)

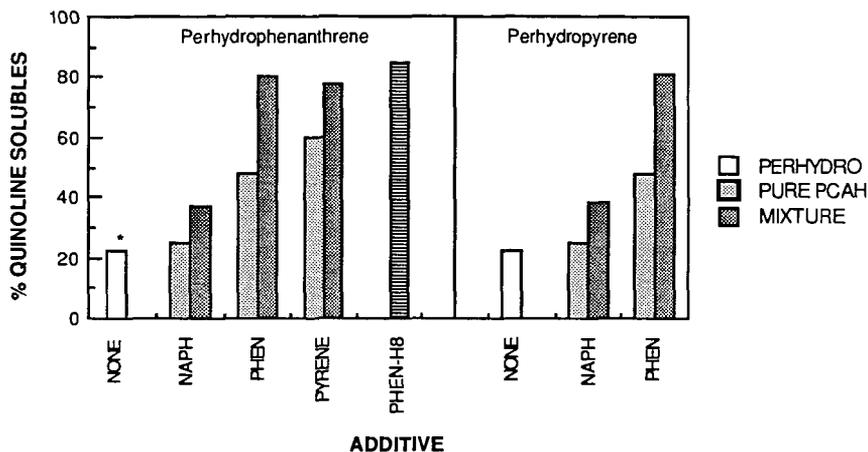


Figure 2. Impact of added PCAH on coal liquefaction in perhydroaromatics. Conversion in 1:1 mixture of perhydroaromatic and aromatic compared with conversion in either pure component. * Upper limit. (Data from Clarke et al., Ref. 3)

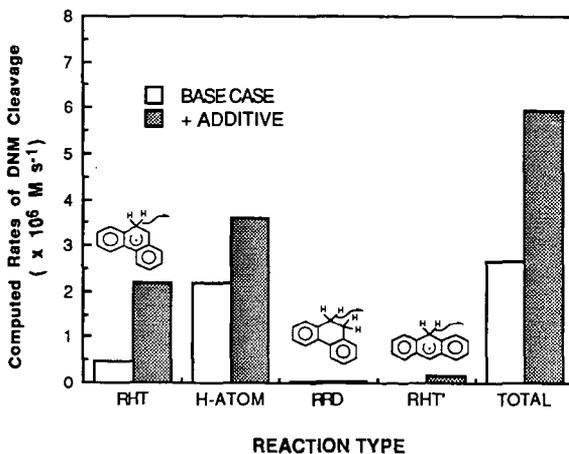


Figure 3: Computed impact of partial replacement of donor with a good acceptor. Base case: PhenH₂/Phen = 10/1; additive is 0.3 M anthracene, replacing an equal amount of dihydrophenanthrene.