

THE CASE FOR INDUCED BOND SCISSION DURING COAL PYROLYSIS

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INTRODUCTION

Most coal pyrolysis models invoke spontaneous thermal scission of inherently weak bonds as the sole pyrolytic reaction leading to depolymerization of coal structures (1).^{*} In this view, bond scission is dependent only on temperature; the only additional chemical factors that impact the "net" cleavage are scavenging and crosslinking of thermally generated radicals, which can be affected primarily by varying heating rates and other factors that affect heat and mass transport. In contrast to this traditional picture, data obtained by various researchers (partly in the context of coal liquefaction), when taken together, provide a strong argument that induced scission of strong bonds plays a significant role during coal pyrolysis. In this paper we attempt to summarize this argument.

The types of bond cleavage occurring during pyrolysis have been obscured in part because of the inherent difficulty of obtaining mechanistically significant pyrolysis activation energies. It is now well appreciated (3,4) that the apparent activation energy for a mixture that decomposes by a sequence of parallel first order reactions can, under conditions of rising temperature, lie below that of any member of the sequence. This factor is evidently responsible for reported activation energies as low, or lower than, 15 kcal/mole. Thus, when coupled with plausible unimolecular scission A-factors ($10^{14.5}$ to $10^{15.5}$) and a 5 to 15 kcal distribution of activation energies, rates measured under non-isothermal conditions have been shown to correspond to mean activation energies of 50 to 65 kcal/mol (5). This result has quite naturally been taken as evidence supporting the original presumption of weak bond thermolysis. However, 50 to 65 kcal/mol activation energies in no way exclude bond scission that is chemically induced by other components in the pyrolyzing substrate. In the following paragraphs, we outline some of the evidence that such induced bond scission can take place under pyrolysis conditions, and show how including them helps explain certain coal conversion phenomena.

EVIDENCE FOR THE OCCURENCE OF INDUCED BOND SCISSION DURING PYROLYSIS

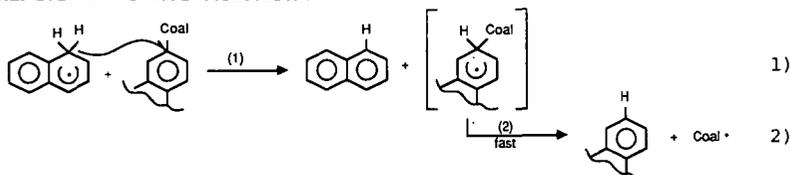
Analogy with Coal Liquefaction. Since the acceptance of the weak-bond-scission/radical-capping model in coal pyrolysis has followed in large part on the acceptance of a similar model in coal liquefaction, and it has now been shown that such a model is inadequate (6-9) for liquefaction, it should also be considered whether the model is inadequate for pyrolysis. The traditional model relegates the liquefaction solvent to a role of merely scavenging thermally generated radicals. However, liquefaction effectiveness of various polycyclic aromatic hydrocarbons (PAH) has been shown very distinctly not to correlate with scavenging, or radical-capping, effectiveness (6,9). For instance, 9,10-dihydroanthracene and its parent hydrocarbon are generally seen to be

*In the most mechanistically complete model of coal pyrolysis presented to date, Gavalas and co-workers have included bond scission induced by ipso attack of H-atoms on linkages to aromatic rings (2). Their suggestion seems to have been either largely ignored, or considered to be a minor side reaction in the production of volatiles.

substantially inferior to dihydrophenanthrene and dihydropyrene, even though dihydroanthracene is a markedly better scavenger. The inferiority of anthracene is most pronounced in the case where the solvent has no hydroaromatic hydrogen to transfer to the coal, but can only assist in shuttling hydrogen from one part of the coal structure to another (10-12). Under these conditions, the traditional mechanism requires in-situ formation of hydroaromatic, which then acts as the capping agent. Dihydroanthracene is not only the most effective scavenger (13) but because of thermochemical and kinetic considerations, is the hydroaromatic most readily formed by hydrogen transfer from coal structures. Nonetheless, it is typically much less effective than either of the other two PCAH.

Since it is clear that the hydrogen being "shuttled" is not serving merely to scavenge fragments of bonds that have already been broken, it is very likely that this hydrogen shuttling is actually inducing bond scission. It is interesting to note that liquefaction under shuttling conditions not only provides the most striking examples of the inadequacy of the traditional liquefaction mechanism, but also resembles coal pyrolysis, in that all of the hydrogen demand must be supplied by the coal itself.

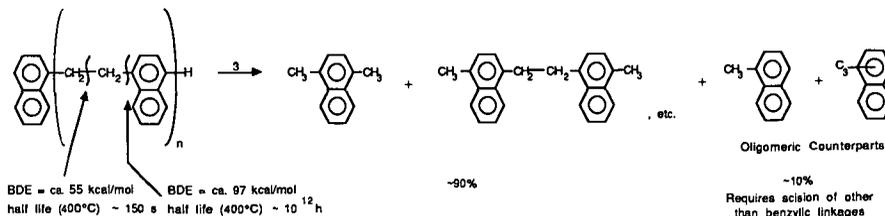
Strong Bond Cleavage by Solvent Mediated Hydrogenolysis. We have used model compound studies (6,8) to show that in hydroaromatic-aromatic PCAH systems, hydrogen-transfer-induced bond scission (hydrogenolysis) of bonds too strong to thermolyze can be significant on liquefaction time scales, even in the absence of H_2 pressure. In addition, we have used hybrid coal/model-compound studies to show (7) that such cleavage tends to be accelerated by the presence of coals, and moreover, to occur by a hydrogen transfer process that does not involve the production of free H-atoms. This "radical hydrogen-transfer" (RHT) occurs in a direct bimolecular process from cyclohexadienyl "carrier" radicals formed from PCAH solvent or coal structures.



The existence of this reaction was for a long time obscured by the fact that it is often in competition with elimination and addition reactions of free H-atoms. Evidence for RHT has now been presented by several groups (14-16). While an addition-elimination sequence can yield the same products as RHT, side reactions (H_2 formation and ring hydrogenation) are associated with elimination addition. For this reason, a shift in the competition between H-transfer by the RHT process and an elimination-addition process can have a substantial impact on the utilization efficiency of solvent or coal hydrogen (6). Thus, we suggest not only that hydrogen-transfer-induced bond scission may be important in coal pyrolysis as well as in liquefaction, but also that the mode of hydrogen transfer may be more critical in pyrolysis, where the available hydrogen is limited to that which can be transferred from the relatively hydrogen-rich portions of the coal structure. The importance of hydrogenolysis mediated by solvent radicals (or coal radicals) moves such radicals from the category of species for which the only goal is to prevent retrograde reactions, to species which can, in addition, be sources of bond cleavage activity.

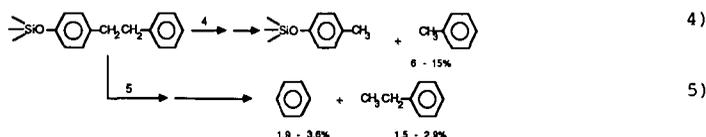
Strong-Bond Scission in Pyrolysis of Coal Models. Direct evidence for induced scission of alkyl-aryl linkages in the nominal absence of solvents can be seen in the pyrolyses of polymeric coal models consisting of aliphatic linkages between PCAH clusters. Solomon and co-workers have pyrolyzed a series of polymers $(-Ar-CH_2-CH_2-)_n$ at 400 to 430°C and analyzed the tars by field

ionization mass spectrometry (17). This analysis revealed that polymeric coal models purposely synthesized to decompose entirely by thermolysis of the weak central bond, provide, in addition, a small but significant amount of product indicative of cleavage of the much stronger aryl-alkyl linkage.

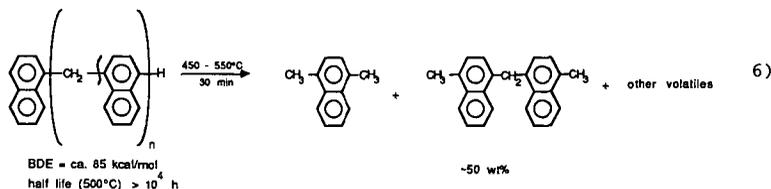


The known strengths of the two bonds (18) are such that at 400°C, the thermolysis half-life of the weaker bond is several hundred seconds, whereas the half-life of the stronger bond would be 10^{10} times longer -- wholly unobservable if thermolysis were the only available cleavage route.

These results with weakly bonded polymers are parallel to those of Buchanan (19) and co-workers who have shown that when bibenzyl is immobilized by bonding to a silica surface, induced bond-scissions become substantially more important than they are in the liquid phase. The yield of benzene and ethylbenzene ranges from about 40 to 70% of the yield of toluene. In other words, for every one to two bibenzyl linkages that break spontaneously, there is another, very strong bond whose scission is induced by hydrogen transfer. As discussed by Buchanan, the restraint provided by the bonding makes radical-radical reactions less likely, and unimolecular reactions such as rearrangement and H-atom elimination more likely. The latter reaction can then lead to hydrogenolysis of an adjacent bibenzyl structure.

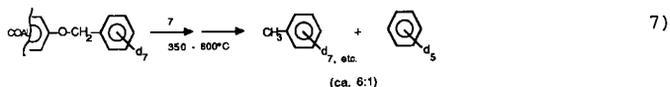


Similarly, earlier work by Van Krevelen (20) on polymers that contained no weak linkages whatsoever had shown that when heated in a nitrogen stream at 3°C/min, these single methylene bridged polymers were roughly half converted into volatile material during the 30 minute passage through the 450 to 550°C temperature range.



For the case of the methylene-bridged naphthalene polymer, where the central linkage has a bond strength of ~ 85 kcal/mol (18), the thermolysis half-life even at 550°C would be $>10^3$ hours.

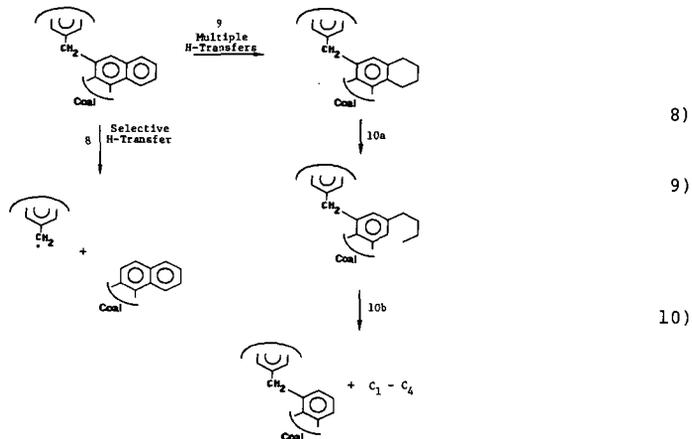
Pyrolysis of O- and C- Alkylated Coals. Various groups have shown that the methylation of coals (17,21), particularly low-rank coals, prior to pyrolysis improves the yields of the volatiles. These yield increases have been attributed to inhibition of retrograde reactions involving phenolic -OH, but they can also reflect an increased contribution from induced bond scission processes. This has been illustrated recently by Stock and co-workers (22) who have examined the product of O- methylated and O- and C- benzylated coals and found not only the expected cleavage (thermolysis) of the weak O-benzyl and C-benzyl bonds, but also the cleavage of the much stronger phenyl-C bond.



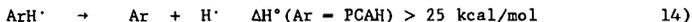
IMPORTANCE OF INDUCED BOND SCISSION

The above results provide a very clear demonstration that induced scission of strong bonds in known structures does take place under pyrolysis conditions. These results suggest, but do not prove, that such cleavages also take place in coals during pyrolysis. However, the pertinent question we have to ultimately consider is whether such cleavage is of any significance to the practice of coal pyrolysis. In the following paragraphs we show that the same competing H-transfer steps we have found to be important under liquefaction conditions can account for striking variations in the yields of oil and gas resulting from modest changes in pyrolysis conditions.

Oil and Gas Yield Variations in Hydropyrolysis. Gorbaty and Maa have reported (27) that the product distribution in a fixed-bed hydropyrolysis is critically dependent upon whether the reaction temperature exceeds the threshold above which there is a pronounced exotherm. The incremental yields obtained by a switch of the pyrolysis gas from N₂ to H₂ go almost exclusively to oil if the temperature remains below this threshold, but go almost exclusively to gas if the threshold temperature is exceeded. These results are shown in Figure 1. As indicated by the authors, the higher temperatures produced in the exotherm evidently result in more ring hydrogenation and ring opening (followed by cleavage of the newly produced side chains), yielding more gas.



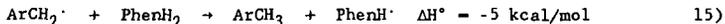
The effectiveness of the aromatic pool in regaining "wastefully" transferred hydrogen is a function of the nature and concentration of the aromatic and the temperature. At a given temperature, the rate of this retrieval of hydrogen increases with increasing aromatic concentration in the solvent (or in the coal if there is no solvent). On the other hand, to the extent that the concentration of aromatic is too low, the non-*ipso* radicals will obtain a second hydrogen (e.g., from another molecule of ArH₂) to yield uncleaved dihydro product. At higher temperatures, the endothermic reactions



are shifted to the right, and any given Ar becomes less effective as a "reservoir" for H-transfer activity. This means that the non-*ipso* radicals will have a greater opportunity to obtain a second hydrogen to form dihydroaromatics. Such dihydronaphthalene-type species are very reactive and will be rapidly further reduced to tetrahydro products. The dihydro and tetrahydro products are then subject to ring-opening and loss of all or part of the newly formed chains as C₁ to C₄ hydrocarbons.

What helps make the shift in incremental yields from oil to gas so dramatic is the fact that the decreasing effectiveness of the aromatic pool with increasing temperature provides the system with marked feedback potential. When the temperature reaches the point where ineffectiveness of the solvent pool in regaining H-atoms allows sufficient ring hydrogenation such that the heat evolved exceeds the fixed-bed heat transfer capability, the temperature begins to rise faster. This rise further decreases the ability of the aromatic pool to regain wastefully transferred H-atoms, ring hydrogenation is further promoted, the temperature goes up still faster, and so on, in an accelerating manner.

Role of Coal Fragments in Induced Bond Scission. All of the results summarized here support, in one way or another, the hypothesis that aromatic/hydroaromatic reaction media, and H₂ as well, serve not only to scavenge coal radicals, but also to generate hydrogen transfer activity. Making the very probable assumption that the connections in coals consist of some weak covalent linkages, which will undergo thermal scission regardless of the reaction medium, and some linkages so strong they will cleave only when induced to do so by hydrogen transfer, it becomes clear that the radicals generated by scission of the weak links have a much more important role to play than merely being "capped" by hydroaromatic species (or H₂). To the extent they are non-hydroaromatic radicals (e.g., benzyl), these radicals typically have no hydrogenolysis activity: they cannot transfer a hydrogen to a cleavable substrate because they cannot, in so doing, form an aromatic system. If not capped, such thermally generated radicals may indeed become involved (as the conventional view would have it) in retrograde reactions. The important point however, and the one not included in most pyrolysis pictures, is that when the scavenger is a hydroaromatic, the capping process actually constitutes a chain transfer step that converts a radical with no hydrogenolysis activity into a radical that can induce hydrogenolysis.



The potential role of coal radicals in providing hydrogenolysis activity suggests that the high reactivity of coals in the initial stages of conversion may result from a "burst" of coal radicals that is large compared to the steady state level of ArH[·] supplied by the hydroaromatic media. If this is the case, then the conversion of inactive, non-donor radicals into ArH[·] carrier radicals (by either the solvent or by hydroaromatic coal species) could help explain the initial high reactivities of coals. If the number of initiating radical species is too high to be quickly disposed of via the normal termination pathways of the medium (i.e., radical disproportionation), then there should be a significant increase in activity. In hybrid studies involving mixtures of coals and model compounds,

we observed (7) that the addition of coal substantially increases the model compound hydrogenolysis rate. At 400°C, the rate in the modest liquefaction solvent, tetralin, was increased by a factor of about forty. In the more effective solvents, dihydrophenanthrene and dihydropyrene, the rate was increased by a factor of two to three. Thus, under the liquefaction conditions of these experiments, some species generated by the coal (presumably free radicals) very clearly were a source of bond cleavage activity, not merely something to be scavenged. In the absence of evidence to the contrary, it is reasonable to assume that the same phenomenon occurs under pyrolysis conditions.

Coal Pyrolysis in Reactive Vapors. An awareness of the triple role of aromatic/hydroaromatic media (radical scavenger, agent for conversion of inactive radicals into hydrogenolytically active radicals, and retriever of wastefully transferred hydrogen) raises questions about the relative merits of two different approaches to augmenting hydrogenolysis activity in coal pyrolysis: the use of high pressure hydrogen and the use of hydroaromatic PCAH vapor.

The use of hydrogen pressure to augment volatiles yields during coal pyrolysis is not a new approach. H₂ is, of course, a thermodynamically powerful reducing agent. However, owing to the strength of the H-H bond, H₂ is kinetically ineffective at low temperatures (in the absence of a catalyst). Unfortunately, the low temperature range of coal pyrolysis (300 to 500°C) is precisely the region in which coals become highly reactive and in which they seem particularly susceptible to oxidative retrograde reactions. In fact, it is already well appreciated (26) that the presence of H₂ actually tends to decrease volatiles yields (relative to pyrolysis in a vacuum)² at temperatures below about 600°C. Consideration of the kinetics of the reaction by which H-atoms are produced from H₂ emphasizes why this is the case.



$$\log k_{16,400} (1 \text{ m}^{-1} \text{ s}^{-1}) = 1.7$$

For Ar = phenyl, this reaction is 16 kcal/mol endothermic (18) in contrast to the analogous "scavenging" reaction shown above (reaction 15), which is 5 kcal/mol exothermic, and at least 100 times faster at 400°C (at equivalent concentrations of the respective "scavengers").

$$\log k_{15,400} (1 \text{ m}^{-1} \text{ s}^{-1}) = 3.8$$

While the hydrogen carrier radical generated (ArH[•]) is not nearly as active as H[•] on a per molecule basis, it, as discussed above, is much more efficient in transferring hydrogen selectively to places where it is utilized for cleavage, and it cannot abstract another H-atom to uselessly form H₂. In addition, in the low temperature pyrolysis region, near-molar concentrations of such PCAH and their hydroaromatic derivatives can be generated at pressures in the vicinity of one atmosphere, whereas, maintenance of 1M [H₂] requires about 800 psi. Finally, the Ar/ArH₂ mixtures are themselves sources of these hydrogenolytically active radicals (by reverse radical-disproportionation (25,26) that can rival in numbers the radicals thermally generated from the coal structures. Thus, it seems likely that heating the coal in the presence of ArH₂/Ar vapors (or with "pre-loaded" Ar/ArH₂) could offer some of the conveniences of pyrolysis, and be, in the 350 to 500°C temperature range, a more effective way of inducing hydrogenolysis in the coal structures than is provided by heating in hydrogen pressure. The recent work of Gorbaty and co-workers (27) will presumably shed some light on the practicality of this approach, as well as providing data that will help to unify the chemical pictures of coal liquefaction and gasification.

CONCLUSION

In summary, experimental evidence now strongly supports the hypothesis that induced cleavage of strong bonds is a significant part of coal pyrolysis as well as liquefaction. Furthermore, conversion results indicate that shifts in the modes of hydrogen transfer affect hydrogen utilization efficiency and product distribution, and that variations in reaction conditions do indeed have an impact on the induced bond scission processes. Therefore we suggest that the most fruitful working hypothesis for coal pyrolysis/gasification research is that such induced bond scissions can be substantial and are subject to manipulation, and assert that attempts at manipulation are more likely to be successful to the extent that we obtain an improved understanding of the chemistry of these cleavage processes.

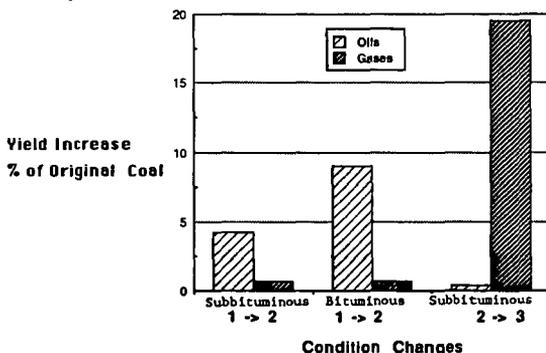
ACKNOWLEDGEMENT

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Each of the three sets of bars should be viewed in isolation from the other two. Each represents the distribution of the additional yields obtained as a result changing from one set of conditions to another.

Cond. 1. 372 → 465°C, 35 min, N₂

Cond. 2. 372 → 465°C, 35 min, H₂

Cond. 3. 372 → 525°C, 85 min, H₂

Taken from the data of Gorbaty and Maa, 1986.

Figure 1. Incremental Yields Resulting from Gas and Temperature Changes in Coal Pyrolysis