

FUNDAMENTAL HYDROGEN TRANSFER STUDIES IN COAL LIQUEFACTION:
UNDERSTANDING THE ANSWERS AND QUESTIONS.

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The goal of our research is to quantitatively understand mechanisms of hydrogen transfer pathways between coal-like structures. Understanding the differences between the various hydrogen shuttling mechanisms will yield valuable insight into the fundamental chemistry of coal hydroliquefaction. We have combined experimental model compound studies with theoretical approaches to gain a quantitative understanding of the hydrogen transfer process involving donor solvents that promote the scission of strong bonds and prevent retrograde reactions. Mechanistic modeling has been utilized for the development of a global model for predicting rates of bond scission for one-, two- and three-ring diarylmethanes. The model is tested by thermal model compound studies with labeled donor solvents. Ab initio studies have been utilized to obtain activation parameters for the novel radical hydrogen transfer pathway, and semi-empirical methods have been used to investigate trends within families of both hydrogen transfer and hydrogen abstraction pathways.

Keyword. Hydrogen Transfer.

Introduction.

The classical model of coal hydroliquefaction has evolved from assuming a passive role for hydrogen donor solvents trapping free radicals formed from the thermolysis of labile bonds, to a model that predicts an active role for hydrogen donor solvents participating in the scission of thermal stable bonds.

Fundamental approaches utilizing model compound studies have provided the impetus for evolution of this model as they provide strong evidence for the importance of hydrogen donor solvents in the scission of strong bonds.¹⁻¹⁰ The philosophy of basic research in coal hydroliquefaction is to gain an understanding of structure-reactivity relationships. Understanding why a change in structure results in a change in reactivity will lead to an intelligent approach to improving hydrogen transfer reactions that control both bond-cleaving and bond-forming reactions.

A simplified picture of the units that hold the structures of coal together is summarized in Scheme I. Thermally labile bonds can cleave homolytically to form stabilized radicals (1); arenes linked by longer alkyl chains can decompose by β -scission following hydrogen abstraction (2); and thermal stable diarylmethanes can be cleaved by β -scission following hydrogen transfer from solvent molecules (3). The goal of our research is to understand the role of hydrogen transfer pathways from donor solvents to coal model structures that can result in the scission of this class of strong carbon-carbon bonds.

Scheme I.



The role of donor solvent in both the homolysis pathway (1), and the radical scission pathway (2) is generally to trap the incipient radicals to prevent retrograde reactions. On the other hand, the donor solvent participates in promoting the scission of strong diarylmethane carbon-carbon bonds (3).

Several of the model compound studies have focused on identifying and quantifying the competing mechanisms that have been postulated to be important hydrogen transfer steps between aromatic structures. The common denominator of all these works is the dynamic exchange of hydrogen transfer reactions between arene structures. This is not surprising, given the early studies that showed deuterium from labeled solvents can be transferred throughout the coal.^{11,12} Hydrogen from the donor solvent, hydrogen gas, and/or from the coal itself is thoroughly scrambled throughout the system. The goal of liquefaction is to have the hydrogen scramble to the appropriate locations to promote bond scission. Thus a fundamental understanding of what controls the hydrogen transfer pathways, from a donor to a receptor, can provide beneficial guidance for experimental process development.

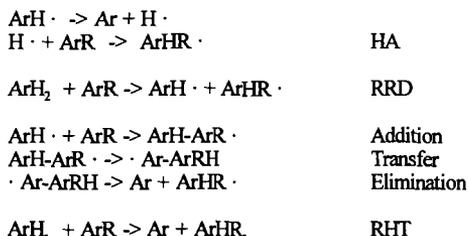
Consideration of both the kinetic and the thermodynamic factors of hydrogen transfer to diarylmethanes leads to two simple questions. *Is hydrogen transfer to the ipso position a necessary requirement for bond scission?* Direct hydrogen transfer to the ipso position of a

substituted aromatic ring is both sterically and thermodynamically less favorable than addition alpha to the substituent. *How can we break only the bonds we want to break?* We want to cleave diarylmethanes and leave the alkyl groups alone to increase the formation of liquids and prevent the formation of light gases.

Thermolysis Questions.

Fortunately, an understanding of structure reactivity relationships can lead to some insight to answer these questions. McMillen and Malhotra^{4d} have reviewed four possible non-ionic mechanisms of hydrogen transfer that could be responsible for the scission of diarylmethane C-C bonds, summarized in Scheme II: (1) free hydrogen atoms (HA), a two-step pathway involving the scission of a hydrogen from a hydroaryl solvent radical followed by addition to the diarylmethane; (2) reverse radical disproportionation (RRD), involving the transfer of a hydrogen atom from the dihydroarene solvent; (3) addition transfer elimination (ATE), involving a multi-step addition of the solvent radical to the diarylmethane, followed by hydrogen transfer, and elimination; and (4) radical hydrogen transfer (RHT), involving the transfer of a hydrogen atom from a solvent radical to the diarylmethane.

Scheme II.



Clearly, there is no lack of potential pathways to make diarylmethanes look like weak bonds; an understanding is needed of what pathways are important under a given set of conditions, and how to optimize the transfer of hydrogens to the appropriate positions that promote bond scission.

These free radical hydrogen transfer pathways are separated into two categories. Because of the product-like (RRD) and reactant-like (HA) nature of the transition state of these two pathways, the activation parameters can be estimated. On the other hand, because of the intermediacy of the transition state of the RHT and ATE hydrogen transfer pathways, the activation parameters are not so easily predicted. For these hydrogen transfer reactions, computational approaches will be necessary to investigate the structure reactivity relationships.¹³ The difficulty in assigning a barrier to these pathways has resulted in some debate as to the significance of the RHT hypothesis.^{4d,e} Although the RHT pathway was suggested to operate under a limited set of conditions,^{1c} it has often been invoked as an important pathway for the scission of a large variety of conditions.¹⁴

Regardless of the pathway, hydrogen is transferred to the arene structures in the presence of donor solvents. In our current work we are concerned with the fate of adding hydrogen, by any pathway, to a nonipso position and if this can result in the scission of strong carbon-carbon bonds.

We have attempted to devise an experiment to quantify how many hydrogen transfers are required to induce bond scission in diarylmethanes. Thermolysis studies of 1,2-dinaphthylmethane (1,2'-DNM) in a perdeuterated donor solvent mixture, dihydroanthracene(d_{12})/anthracene(d_{10}) results in the scission of the diarylmethane to yield both naphthalene and methylnaphthalene (ca. 5% conversion, 100 minutes, 400°C). Analysis of the products and reactants by GCMS reveals several interesting observations. The most obvious is the reduction of anthracene by the dihydroanthracene as we previously observed.^{4f} Reduction of the 1,2,3,4-positions of anthracene occurs by a series of RRD and hydrogen abstraction steps. Analysis of the remaining 1,2'-DNM shows more deuterium incorporation into the diarylmethane than was expected from exchange at the benzylic positions. Therefore, hydrogen (labeled as deuterium in this experiment) is transferred to the arene rings of the diarylmethane from the donor solvent without the scission of any carbon-carbon bonds. Analysis of the product naphthalene shows that, on average, more than one deuterium is incorporated in the naphthalene cleavage product. If direct ipso hydrogen transfer was the only operating hydrogen transfer mechanism, only one deuterium would have been detected in the naphthalene product. However, because more than one deuterium per scission product was detected, something in addition to ipso displacement must be competing.

This should not be surprising if the probability of adding a hydrogen to the ipso

position is considered versus the probability of adding a hydrogen to any other position. To illustrate, consider the case of hydrogen transfer by a reasonably selective mechanism (RRD or RHT), to the ipso position of diphenylmethane. Several factors reduce the probability of ipso hydrogen addition (Figure I). One source of discrimination between the ipso and nonipso positions is the steric bulk of the donor, either a dihydroarene (RRD) or a dihydroaryl radical (RHT). Additional thermodynamic factors are against ipso addition. The adduct formed by addition of hydrogen γ or β to the ipso position yields a tertiary radical that is more stable than the secondary radical formed by addition to the ipso position. Finally, consideration of statistics suggests there are several more nonipso positions, 2,3,4,5 or 6-position. A conservative estimate suggests addition of a hydrogen atom to the nonipso position will occur ten times more frequently than addition to the ipso position. It could even be argued that there is a higher probability that the "less selective" free hydrogen atom pathway will more likely add to the ipso position of a substituted arene because this pathway is least affected by the steric or the thermodynamic constraints.

If, as we have argued, the hydrogen is more likely to be transferred to a nonipso position, to understand the complete picture we must understand the fate of the nonipso hydrogen addition adduct. A more complete scheme of hydrogen transfer, including the addition to nonipso positions, is shown in Figure II. Depending on the reaction conditions, there are two possibilities for the nonipso adduct. At higher donor (dihydroarene) concentrations it is possible to trap the adduct. Abstraction from the solvent to produce a reduced arene, path (e), results in lowering the bond energy of the diarylmethane to the ballpark of the thermally labile diarylethane type bonds.¹⁵ At low donor (dihydroarene) concentration, scission of the hydrogen atom will dominate the radical termination pathways. In this case, although we may not have started with a free hydrogen atom, we may need to account for free hydrogen atom chemistry for a complete picture.

If the nonipso adduct is not trapped something must be done to make efficient use of the hydrogen atom donated from the solvent mixture. One approach that has been used at low donor concentrations is to add a good hydrogen atom trap. Hydrogen atoms add to arenes more readily than abstract from dihydroarenes.^{1b,7a} If anthracene is added to the reaction mixture, the hydrogen can be stored for re-use. Radical disproportionation of the hydroaryl radical generates a dihydroarene donor solvent.

It remains to be determined if the excess deuterium observed in the 1,2'-DNM thermolysis studies is due to bond scission by the reduction (pathways b, e, and f) shown in Figure II or due to inefficient hydrogen transfer (pathways b, and d, or RHT, in competing with ipso addition). Answering these questions will provide additional insight into improving the efficiency of hydrogen transfer and best utilization of hydrogen donor solvents.

Catalysis Questions.

It has also been reported that iron catalysts promote the scission of diarylmethanes at lower temperatures than thermal solvent pathways.¹⁶ We have found that alkylarenes are reduced with no apparent loss of the alkyl group. For example, we have found that the catalytic reaction of 1-methylnaphthalene in dihydrophenanthrene results in the formation of 1-methyltetralin; no naphthalene scission product was detected. On the other hand under the same reaction conditions, 1-benzyl naphthalene and its derivatives yield only scission products with no apparent reduction.

Studies investigating the relative rates of bond scission in a series of diphenylmethanes suggest a mechanism that may involve either a two-step, electron transfer followed by reduction of the radical center or a proton transfer from the catalyst to the substituted arene (Figure III). A mechanism involving ipso hydrogen transfer from the catalyst to the arene is tentatively ruled out because we would have observed little selectivity between the scission of either the methyl or the benzyl substituent if hydrogen transfer to the ipso position were rate limiting.¹⁷ We prefer the two-step electron transfer-hydrogen atom transfer mechanism to generate the intermediate cation. Compared to the radical mechanism where the loss of a benzyl radical is only ca. 10 kcal/mol lower than loss of methyl radical, there is a substantial difference in scission by the ionic pathway. The difference between scission of a benzyl cation and scission of a methyl cation could be as high as 70 kcal/mol.

Wei et al.¹⁸ have compared the decomposition of dinaphylmethane with the decomposition of dinaphthylethane. A similar mechanism could be proposed for their hydrocracking catalyst. They only detected scission when a stabilized leaving group was present, e.g. dinaphylmethane to naphthalene and methylnaphthalene. In the absence of a stabilized leaving group, e.g. dinaphthylethane, they observed mostly reduction, tetralin derivatives.

Conclusions.

Hydrogen transfer is extremely dynamic. It is hard to imagine a magic catalyst or smart solvent that can selectively add a hydrogen to the ipso position of a diarylmethane.

Hydrogen will be transferred by one or more pathways several times before finally promoting scission of strong bonds.

We have attempted to answer two questions in our recent work: (1) Is hydrogen transfer to the ipso position a necessary requirement for bond scission? and (2) How can we break only the bonds we want to break? We have outlined a multistep hydrogen transfer scheme, given the high probability of nonipso hydrogen transfer, that results in a reduced diarymethane adduct capable of homolytic scission at coal liquefaction temperatures. Both the catalytic ionic pathways and the thermal reduction pathways permit the scission of stabilized benzylic radicals without requiring the scission of less stabilized alkanes.

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