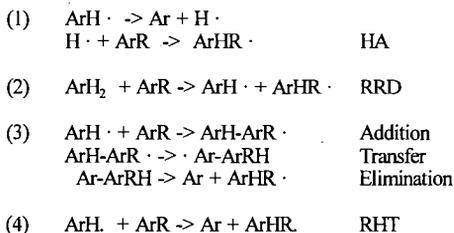


HYDROGEN EXCHANGE PATHWAYS BETWEEN ARENES AND DIHYDROARENES: AN EXPERIMENTAL AND MECHANISTIC MODELING STUDY OF HIGH TEMPERATURE HYDROGEN TRANSFER PATHWAYS.

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Introduction

One of the major areas of interest in thermal hydroliquefaction involves the mechanisms of hydrogen shuttling by aromatic/hydroaromatic donor solvents to coal structure, engendering the scission of thermally-stable alkylaromatic linkages. Derbyshire et al.¹ and McMillen and Malhotra² were among the first to recognize that hydrogen donor solvents can play an active role in the scission of thermally stable C-C bonds in coal structures. At least two "conventional" hydrogen-transfer pathways, hydrogen atoms (HA) and reverse radical disproportionation (RRD), and two "unconventional" hydrogen transfer pathways, radical hydrogen-transfer (RHT)³ and addition-transfer-elimination,⁴ could play a role in the shuttling of hydrogen from donor solvent to the ipso positions of substituted aromatic linkages in coal structures. It is unreasonable to assume that any one of these pathways is responsible for all solvent-engendered bond scission. Depending on the reaction conditions, one pathway may be more dominant than the others, or several of them could contribute simultaneously. A quantitative understanding of competing hydrogen-transfer pathways between aromatic structures can yield valuable information regarding the efficient cleavage of bonds in coal structures during hydroliquefaction. It is the goal of this work to quantify the importance of the conventional hydrogen-transfer pathways and make qualitative predictions regarding the unconventional pathways.



We have undertaken mechanistic kinetic modeling (MKM) studies and experimental thermolysis studies of model compounds to quantify the importance of individual hydrogen-transfer pathways involved in the scission of alkyl-arene C-C bonds in diarylmethanes as a function of donor solvent composition.⁵ In this paper, we report the role of hydrogen-transfer pathways in the aromatic/hydroaromatic solvent mixtures naphthalene/dihydronaphthalene (Nap/NapH₂), phenanthrene/dihydrophenanthrene (Phen/PhenH₂), anthracene/diidoanthracene (An/AnH₂), and cyclohexadiene/benzene (Ph/PhH₂) for promoting bond scission in a family of diarylmethanes (Ar-R)-diphenylmethane (PhCH₂-Ph), 1-benzyl-naphthalene (PhCH₂-Nap), 9-benzylphenanthrene (PhCH₂-Phen) and 9-benzylanthracene (PhCH₂-An).

The results of this work will 1) show the significance of the role of free hydrogen atoms and 2) question the necessity of invoking the radical hydrogen-transfer pathway in promoting c-c bond scission in alkylarenes.

Results and Discussion

One of the advantages of MKM is the ability to quantify individual reaction pathways that compete from the same intermediate or yield the same products. It is a challenging experimental task to separate the amount of alkylarene bond scission by competing RRD and HA pathways. This difficulty has led to ambiguous results regarding the role of solvent-induced bond scission. MKM permits "computer labeling" studies to quantify each competing pathway. The activation barriers for the two conventional hydrogen-transfer pathways, HA and RRD, can be estimated to within a few kcal/mol because of the "product" like or "reactant" like nature of the transition state. On the other hand, there is no a priori means to estimate the intrinsic activation barriers for the two unconventional hydrogen-transfer pathways, ATE and RHT. Theoretical approaches and rigorously-designed experiments must be undertaken to quantitatively evaluate the feasibility of competing unconventional hydrogen transfer pathways.⁶

The Model. A mechanistic model composed of the free radical hydrogen-transfer pathways, initiation, termination, hydrogen scission, abstraction, addition, and reverse radical disproportionation, was developed for each mixed-solvent system and diarylmethane substrate (Scheme I). Arrhenius rate parameters were derived from the literature values of the thermochemical estimates of the heat of formation (ΔH_f) of the products, reactants, and intermediate radicals.⁷ We utilized the regimen of Malhotra and McMillen^{3a} and Manka and Stein⁸ to calculate the temperature-dependant rate for each individual reaction step. For concise introduction, we separate our model in three sections, 1) initiation and termination events, 2) efficient utilization of solvent and bond scission by HA and RRD pathways, and 3) inefficient utilization of solvent.

The initiation pathway utilized in this modeling study is the RRD between the dihydroarene and arene solvent molecules. Only radical disproportionation was considered as a termination event in our model since solvent derived radical coupling products have been shown to be unstable at temperatures above 350°C.⁹

Efficient solvent utilization pathways are defined as pathways leading to the scission of C-C bonds by RRD and H atom pathways. The rate determining step of the two-step HA pathway is scission from the hydroaryl radical. Addition of the hydrogen atom to an arene ring is not expected to be very selective relative to hydrogen transfer by the RRD pathway. Hydrogen atom addition to the solvent will also occur in competition with hydrogen transfer to diarylmethanes. Thus hydrogen from the solvent can be consumed without the scission of C-C bonds, and in some solvent mixtures is predicted to dominate the hydrogen-transfer chemistry.

To compare the rate of product formation from the H atom pathway to the RRD pathway, we utilized a computer "label" of the products arising from each competing pathway. In this way, competitive pathways involving the same intermediates can be quantitatively predicted. For example, we "label" the alkyl-arene bond-scission precursor, ipso addition of a hydrogen atom by to the alkyl position of Ar-x, arising from the RRD pathway as ArXH (equation 14), whereas ipso addition of a hydrogen atom by to the alkyl position of Ar-x arising from the HA pathway, gives ArxH (equation 4). Both "ipso adducts", ArXH and ArxH, are "chemically" the same intermediate; they cleave at the same rate to yield the scission product, labelled RRD(H) (equation 18) and HA(H) (equation 17) respectively. In this manner, we can account for the yield of scission by each competing pathway even when the same intermediate is involved. To calculate the relative rates of solvent-induced scission of Ar-x by each pathway, we compared the predicted yield of the scission product as a function of thermolysis time. Thus, the percent C-C bond scission by H atom pathway = $[HAH] / ([HAH] + [RRDH])$.

Scheme I. Example of kinetic hydrogen-transfer pathways in An/AnH₂

initiation/termination					
1	AnH ₂ +	An	>	AnH +	AnH ₂
2,	AnH +	AnH	>	AnH ₂ +	An
H atom pathways					
4,	Anx +	H	>	AnxH	ipso
5,	Anx +	H	>	AnHx	nonipso
6,	AnHx		>	Anx +	H
7,	AnH		>	An +	H
8,	An +	H	>	AnH	
9,	AnH ₂ +	H	>	AnH +	H ₂
10,	AnH ₂ +	An	>	HAn +	AnH
11,	HAn +	AnH ₂	>	H ₂ An +	AnH
12,	H ₂ An +	AnH ₂	>	H ₂ An +	AnH
13,	H ₂ An +	AnH ₂	>	H ₄ An +	AnH
RRD					
14,	AnH ₂ +	Anx	>	AnH +	AnXH
15,	AnH ₂ +	Anx	>	AnH +	AnHx
16,	AnH ₂ +	AnHx	>	AnH ₂ x +	AnH
scission					
17,	AnxH		>	AnH +	HA(H) HA
18,	AnXH		>	AnH +	RRD(H) RRD
19,	AnH ₂ x		>	AnH +	RED/C(H) nonipso

Examination of Table I clearly shows the importance of free hydrogen atoms in the scission of diarylmethane coal linkages. The only clear case of C-C bond scission by the RRD pathway is in An/AnH₂ solvent mixtures. This can be explained by the stability of the 9-hydroaryl radical. Table II lists the predicted relative total rate of diarylmethane bond scission (the sum total of both RRD and H atom contributions) in the series of solvent mixtures for each substrate, giving

an indication of the "best" solvent for a given diarylmethane structure. A comparison of bond-induced scission of Nap-CH₂Ph in An/AnH₂ versus Phen/PhenH₂ illustrates the selectivity differences between the HA and RRD pathways. The model predicts nearly equal rates of solvent-induced scission; however, the selectivity of bond scission is expected to be greater in An/AnH₂ because of the contribution bond scission by the more selective RRD pathway. McMillen and Malhotra^{3a} have observed that although there is very little difference in the rate of bond scission of 1,2-dinaphthylmethane in Phen/PhenH₂ and An/AnH₂ solvents, there is a substantial difference in the observed selectivity. They suggest that the difference in selectivity is due to the operation of the RHT pathway in An/AnH₂ solvents; however, our current analysis suggests that the increase in selectivity is due to the operation of the RRD pathway in An/AnH₂ solvents.

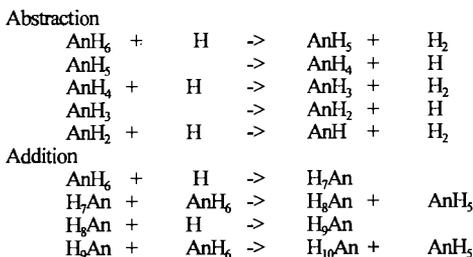
EXPERIMENTAL STUDIES.

To test both the rate and selectivity predictions of our mechanistic model of hydrogen transfer pathways from dihydroarenes to diarylmethanes, we have utilized experimental thermolysis studies of 1,2-dinaphthylmethane (DNM) in AnH₆ and An/AnH₂ solvent mixtures. Our model suggests that cyclic olefins, e.g. AnH₆, will be faster and less selective than An/AnH₂ solvent mixtures with less selectivity in the solvent-induced scission of DNM.

Cyclic Olefins. 1,4,5,8,9,10-Hexahydroanthracene AnH₆.

The predicted rate of bond scission in Ph/PhH₂ solvent mixtures as shown in Table II suggests that cyclic olefins are a special class of dihydroarenes donor solvents. Bedell and Curtis¹⁰ have demonstrated that cyclic olefins provide enhanced liquefaction yields relative to their dihydroarene isomers. However, we note a chain-decomposition pathway of the cyclic olefins can limit the efficiency of C-C bond scission by this family of donors as shown in Scheme II.

Scheme II Chain Decomposition Pathways of Cyclic Olefin Donor Solvents.



Thermolysis of neat AnH₆ at 380°C results in a variety of hydroanthracene isomers with total consumption of the cyclic olefin in less than 20 minutes. The conversion of 1,2-dinaphthylmethane (DNM) in hexahydroanthracene at 380°C is dependant on the starting concentration of DNM; at lower DNM concentrations, hydrogen atoms add competitively to the solvent AnH₆. Thermolysis of DNM in AnH₆ results in a 20-30% consumption of DNM in the first 20 minutes followed by a much slower conversion.¹¹ The observed selectivity of bond scission as measured by the yield of 2-Methylnaphthalene/1-Methylnaphthalene (1.6) is what is expected for a free-hydrogen-atom scission pathway.^{3a}

Dihydroarene. Anthracene/9,10-Dihydroanthracene An/AnH₂

Thermolysis of mixtures of An/AnH₂ at temperatures above 380°C result in a dynamic exchange of hydrogen atoms between the anthracene structures with very little hydrogen formation of hydrogen gas. The process results in a shift of hydrogen from 9,10-dihydroanthracene (AnH₂) to anthracene to yield 1,2,3,4-tetrahydroanthracene (AnH₄). Formation of the AnH₄ has been suggested to occur by a series of RHT steps from AnH• to the outer ring of anthracene.¹² However, we have found that the time-dependant formation of AnH₄ can be fit to a series of RRD steps without the need to invoke the RHT pathway.

Thermolysis of DNM in mixtures of An/AnH₂ yields <1% consumption in the first 20 minutes (as compared to >30% in AnH₆). The selectivity of bond scission as measured by 2-Methylnaphthalene/1-Methylnaphthalene is higher, between 4-6. As predicted by our MKM results, the selectivity does not change substantially as the ratio of An/AnH₂ is increased as has been previously suggested^{3a}. However, the selectivity is predicted to be very sensitive to the addition of a diluent, such as biphenyl (BP). Adding BP lowers the rate of bond scission by the RRD pathway, but has little effect on the rate of scission by the HA pathway. The net result of the dilution studies is thus a predicted decrease in rate as well as selectivity. The results of

the thermolysis study and the predictions of our mechanistic model are shown in Figure I. A set of control experiments was performed to investigate the occurrence of secondary thermolysis events. When a small amount of tetralin, 10% by weight, was added to the starting reaction mixtures of DNM in An/AnH₂, we found that the tetralin was consumed under the reaction conditions at high An/AnH₂ solvent ratios. This is most likely due to the low concentration of AnH₂ donor available for capping the radicals formed by the solvent induced scission. Formation of tetralin products can arise from adding of hydrogen to nonipso positions of DNM.^{3c} If these reduced products are consumed in secondary events under the reaction conditions, e.g. low donor concentration and long reaction times, one could be led into believing that a change in hydrogen-transfer pathways was leading to a more efficient utilization of hydrogen from the donor solvent when in fact, the same hydrogen-transfer process could be in operation but the hydrogen is recycled.

Conclusions. MKM and thermochemical kinetic estimates predict that hydrogen atoms dominate the chemistry of strong bond scission. Cyclic olefins are predicted by MKM and have been found experimentally to be extremely rapid with little selectivity and only limited by competition with self reactions consuming the solvent.

All model compound studies that we have examined¹³ can be explained by conventional hydrogen transfer pathways when consideration is given for the uncertainty in estimating the arrhenius-rate parameters. We are gratified that the results from our simple mechanistic model, utilizing only free hydrogen atoms and reverse radical disproportionation pathways, reproduced our own experimental observations regarding relative rates and selectivities of diarylmethane alkyl-arene bond scission in hydroarene donor solvents as well as other published observations.

While the uncertainty in the thermochemical data of free radical pathways does not rule out the possibility of some contributing RHT type pathway, it does require faith to propose a novel hydrogen pathway such as RHT based solely on MKM results. Until either rigorous theoretical approaches or direct, unambiguous experimental evidence is obtained, we suggest caution in invoking the RHT pathway between arenes. On a note of RHT optimism, we suggest that further studies of the RHT pathway should be investigated when polarized transition states are possible.¹⁴

Experimental. All solvents and reagents were purchased from Aldrich. Anthracene was sublimed, and dihydroanthracene was recrystallized three times from 95% ethanol. Thermolysis experiments of mixtures containing anthracene and dihydroanthracene were prepared in sealed pyrex tubes. Stock mixtures 1/1, 1/5, 5/1 wt/wt were prepared in bulk by grinding the pure compounds together with a roller-ball mixer. **Mechanistic Modeling.** Acuchem¹⁵ utilizes a variable step integrator to solve stiff integration problems. Temperature dependent molar density of anthracene was obtain from the API reference guide available through Chemical Abstracts online service in file DIPPR.

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Table I. Predicted contribution of scission by H-atom pathway, balance RRD. 400°C (Ar/ArH₂ 3/1) 10% by weight substrate Ar-R.

	Ph/Ph ₂ °	Nap/NapH ₂	Phen/PhenH ₂	An/AnH ₂
Ph-R	100	100	100	98
Nap-R	100	99	99	29
Phen-R	100	69	82	13
An-R	76	58	56	0

Table II. Relative Rate of scission by RRD and H atom pathways. 400°C (Ar/ArH₂ 3/1) 10% by weight substrate Ar-R.

	Ph/Ph ₂	Nap/NapH ₂	Phen/PhenH ₂	An/AnH ₂
Ph-R	3100	40	6	1
Nap-R	1900	80	10	6
Phen-R	1560	100	13	17
An-R	100000	2300	650	12600

Figure I. Mechanistic kinetic model predicted and experimental observed selectivity of Bond Scission. Thermolysis of DNM in Anthracene/Dihydroanthracene (An/AnH₂) with (w) and without (w/o) biphenyl and a cyclic olefin 1,4,5,8,9,10-Hexahydroanthracene (AnH₆).

