

CLEAVAGE OF BENZYLAROMATICS AND THEIR RELEVANCE TO COAL CONVERSION

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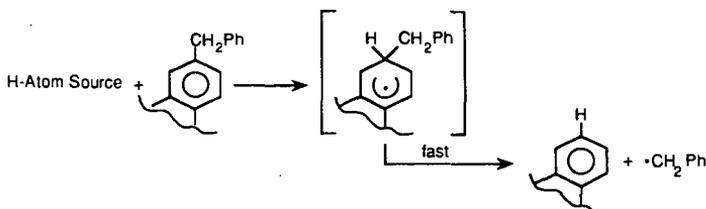
INTRODUCTION

The modes by which bonds are cleaved during coal liquefaction continues to be a subject of controversy, not only because the nature of the "critical" linkages in coals are not known with any certainty, but also because the detailed nature of some of the hydrogen-transfer reactions that lead to cleavage is still not fully understood. It is now fairly well agreed that ipso hydrogen displacement not involving free H-atoms can result in the cleavage of some coal-like structures under liquefaction conditions (1-8). However, it is still a matter of debate whether such cleavage is (a) general for linkages to aromatic rings, (b) significant for coal liquefaction, and (c) takes place by the radical hydrogen-transfer (RHT) process, as has been claimed (1). In this paper we present data that indicate that cleavage not involving free H-atoms (i.e., a solvent-mediated hydrogenolysis) is general for linkages to aromatic rings (though at rates which vary widely with the nature of the ring system). We also discuss, in the light of this recent data, some previously reported results that suggest such cleavages are indeed significant in coal liquefaction. Finally, we discuss those mechanistic alternatives to an actual RHT process that have not been eliminated by previous results. We defer all discussion of RHT itself or its specific mechanistic alternatives until the questions of generality of solvent mediated hydrogenolysis and its relevance to coal liquefaction have first been considered.

RESULTS AND DISCUSSION

Cleavage of Benzylaromatics. Figure 1 shows the measured rates of ipso-displacement of benzyl groups from arenes containing one to four aromatic rings in a 1:1 mixture of anthracene and 9,10-dihydroanthracene at 400°C. These experiments were performed in sealed fused-silica ampoules containing 10 wt% substrate in a 1:1 anthracene/dihydroanthracene mixture, and were analyzed by GC-MS. The measured rates are expressed as defined first-order rate constants. Displacement was observed in all cases, with the reaction becoming progressively more facile as the ΔH° for H-atom addition to the aromatics becomes more negative. While this cleavage is indeed extremely facile for alkyl-anthracenes and -pyrenes, as has recently been noted by several authors (4,6,7,11), it is clear from the data in Figure 1 that it is general for substituted aromatics, rather than unique to pyrene and anthracene type structures as has been suggested (6).

The defined first-order rate constants increase by almost four orders of magnitude (a factor of 6×10^3) in going from diphenylmethane to 1-benzylpyrene. This sensitivity is very similar to that observed by Futamura and coworkers (7) for reaction of diarylmethanes in tetralin, and is far greater than would result from addition of highly reactive free H-atoms to the respective arenes to give the cyclohexadienyl radical cleavage intermediates. Reported H-atom addition rates (9) give an Evans-Polanyi factor less than 0.2 and an anticipated rate increase of less than a factor of ten for free H-atom addition to benzylaromatics in this series. Thus, there is little doubt that some active H-donor other than H-atom itself is transferring hydrogen to the closed-shell reactants to generate the necessary cyclohexadienyl radical intermediate.



Scheme 1. Cleavage of Benzylaromatics by H-Atom Transfer.

Transfer of an H-atom directly from a dihydroaromatic (i.e., an RRD process) would certainly exhibit high selectivity (higher even than RHT). However, the rough similarity of cleavage rate constants observed in solvents having vastly different C-H bond strengths, such as dihydroanthracene and dihydrophenanthrene (1,2,11,22), and even tetralin (7), have already demonstrated that RRD cannot, in all cases, constitute the stoichiometric and rate-determining H-transfer step.

Significance for Coal Liquefaction. An explicit determination of the importance of cleavage by ipso-desubstitution in coal liquefaction, as noted above, is not possible at the present time, since the nature of the critical linkages broken during liquefaction cannot be determined with any certainty. However, as we have previously pointed out, (a) the ability of hydroaromatics to engender hydrogenolysis even in the absence of hydrogen pressures and catalysts, (b) the effectiveness of these known hydrogenolysis agents in coal liquefaction, and (c) the ineffectiveness of pure "scavengers", such as toluene, ethylbenzene and indane, together strongly suggest that hydrogenolytic cleavage of strong bonds is important in coal liquefaction (1,11,12-15). In addition to this descriptive evidence, we have shown several instances where the incorporation of strong-bond cleavage into the liquefaction mechanism pictures enables one to rationalize, and in some cases (15) even predict, coal liquefaction behavior that defies interpretation if one is limited to the traditional weak-bond scission picture of liquefaction. Studies by Zabransky and Stock (16) on coals with various structures grafted onto them very clearly showed that scission of strong bonds induced by the system was competitive with scission of the weak bonds.

The importance of hydrodealkylation has been questioned on the grounds that it is generally a very slow reaction and that other reactions, most notably H-abstraction-- β -scission, can also result in cleavage of strong bonds. Recently, Ceylan and Stock (17) have reported that demethylation of 1,3-dimethylnaphthalene in tetralin/coal mixtures occurs only to a minor extent (~1-4%) in two hours at 400°C, and is much slower than the H-abstraction-- β -scission cleavage of 1,3-diphenylpropane (~35% at 400°C in 30 min.). We do not disagree with these results. Indeed, we find the rates reported by Ceylan and Stock for demethylation of 1,3-dinaphthylmethane to be in good agreement with those we had reported for the decomposition of 1,2-dinaphthylmethane (1,12).

However, in trying to judge whether hydrodealkylation is a significant bond cleavage mode in liquefaction, we must remember that the H-abstraction-- β -scission chain decompositions cannot be the critical bond cleavages that occur during coal liquefaction. H-abstraction-- β -scission cleavages are recognized (5) to be very facile at 400°C, even under neat conditions, and are known not to benefit significantly from tetralin or other hydrogen donors. This type of bond cleavage makes the aliphatic portions of crude petroleum easy to thermally crack even in the absence of H-donors, but it does not lead to substantially increased distillate production rates in the presence of donors or other added sources of hydrogen (18,19). This behavior is of course in stark contrast to that of coals, whose liquefaction benefits enormously from "donor" solvents. Thus, while bond cleavages of the H-abstraction-- β -scission type may indeed be more facile than the typical hydrodealkylation reaction, they are not necessarily the important category of cleavage. By the very fact that ipso desubstitutions sometimes occur only at modest rates and primarily in the presence of favorable reagents, they might properly be judged to be more "critical" than those cleavages which are more facile, and occur anyway.

Furthermore, the rates of hydrodealkylation reactions are highly dependent on the nature of the aromatic ring system to which the linkage is connected, as shown in Figure 1. In addition to the effect of ring size, illustrated by the data in Figure 1, there are the steric and electronic effects of other substituents, notably alkyl and hydroxyl groups. In previous work involving hydroquinone-promoted dealkylation (20), we had observed that in dihydroanthracene the demethylation of 2-methyl-1-naphthol is ~10 times faster than that of 2-methylnaphthalene. Given the degree of phenolic substitution on aromatic ring systems in bituminous and lower rank coals, the cleavage of alkyl linkages to any given naphthalene ring system in a coal is very likely to be significantly higher than that of methylnaphthalene. For instance, had Ceylan and Stock used a methylnaphthol as their probe molecule, we anticipate they would have observed 20 to 30% demethylation in two hours at 400°C in their tetralin-coal-resid mixtures.

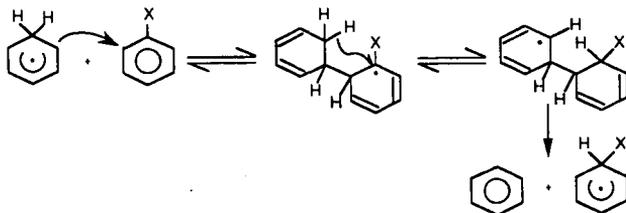
Finally, the cleavage rates for low molecular-weight model compounds are not necessarily indicative of how that same bond type will behave in a polymeric matrix such as coal. We have recently described (13) the "liquefaction" of a bibenzyl-type polymer, poly(1,4-dimethylenenaphthalene), in which the bond scission by hydrodealkylation was observed to be much faster than we had anticipated on the basis of monomeric model compound measurements. Furthermore, the net rate of spontaneous scission (homolysis) of the weak central bond was found to be much slower than one would anticipate from non-polymeric model compound measurements. We rationalized this latter observation by suggesting that the polymeric matrix provides an effective cage in which recombination of spontaneously produced benzylic radicals is drastically reduced. In contrast, bond scission by hydrodealkylation is a process not so easily reversed (since reversal involves an activated radical addition process to produce a highly unstable cyclohexadienyl radical). In fact, it appears that strong bond scission is enhanced in the polymeric system. Most likely, this is because every act of scavenging of polymer fragments by the donor dihydrophenanthrene produces a 9-hydrophenanthryl radical, which is capable of engendering hydrodealkylation, in the vicinity of the polymer. Regardless of the correctness of these explanations, the experimental result was that a hydrodealkylation expected to be some 300 times slower than a weak-bond homolysis had become, in the polymeric system, roughly as fast (13).

For all of the reasons cited in the above paragraphs, we assert that the fact that non-polymeric, unhydroxylated, two-ring probe molecules cleave at the rate of only a few percent per hour does not constitute convincing evidence that cleavages by ipso-substitution are unimportant in coal liquefaction. On the contrary, the other evidence reiterated above warrants the acceptance, at least as a working hypothesis, of the proposition that ipso-displacement by hydrogen constitutes an important part of coal conversion under liquefaction and coprocessing conditions. Given this conclusion, it becomes more than a mere academic exercise to determine in greater detail how the hydrogen transfer which induces this cleavage is taking place.

The Mechanism of Solvent-Mediated Hydrogenolysis. In the purely radical realm, several pathways for transfer of hydrogen leading to strong-bond cleavage have been considered (1,2,4,6,21,22). These pathways include radical hydrogen-transfer (RHT), reverse radical-disproportionation (RRD), also called "molecule-induced homolysis," concerted transfer of H₂, and a multi-step process in which the hydrogen atom source is the same cyclohexadienyl radical carrier species that would be the hydrogen atom donor in RHT itself. Another alternative that cannot be categorically excluded is an electron-transfer-proton-transfer sequence. Although we have been unable to find definitive evidence that would rule out this possibility, we consider it unlikely in systems where both the donor and acceptor are hydrocarbons.

Reverse radical-disproportionation has in some cases (i.e., those with 9,10-dihydroanthracene as the donor and high concentrations of substituted anthracenes as the acceptor) been shown (22) to constitute the stoichiometric hydrogen-transfer step, but with other common donor components, such as 9,10-dihydrophenanthrene and 4,5-dihydropyrene, RRD has been shown (1,2) not to be a major contributor. Similarly, thermodynamic requirements make a concerted transfer of H₂ much slower than sequential transfer in most cases of interest here (1,23). We have also previously presented evidence that a three-step indirect transfer process, such as that depicted in Scheme 2, is not responsible for the observed cleavage (1). However, recent experiments and calculations (6,8) have also raised additional questions (at least in the experimentally and computationally accessible systems) about the specific direct transfer route we

had previously invoked (RHT). Therefore, in the paragraphs below, we reexamine the principal remaining possibility, namely the indirect route.



Scheme 2. Three-Step H-Transfer Mechanism

H-transfer by a Multi-Step Process. This route is comprised of three known elementary reactions: radical addition, intramolecular H-atom abstraction, and β -scission. Because this was a reasonable alternative to the invoking of a new reaction in RHT, and because it had been previously suggested as a likely alternative (21), we discussed this possibility in detail in an earlier paper (1). At that time we ruled it out on the basis of two principal considerations. First, ipso H-transfer by an indirect route requires initial radical-addition at some position other than ipso, usually ortho or para to the ipso position, depending on whether the donor radical is of the 9-hydrophenanthryl type or the 9-hydroanthryl type. In some cases this addition would be extremely electronically unfavorable, because ortho or para is a fused ring position. Second, because reversal of the initial addition is expected to be many orders of magnitude faster than intramolecular H-abstraction (1), we would anticipate many initial additions to different sites (i.e., not just those o- or p- to the substituent), including ipso attack. Ipso attack should then lead to radical displacement products, which were often not observed. Since the recent experimental and theoretical work of Autrey and Franz (8), and of Freund et al. (6), have raised additional questions about the viability of the RHT pathway itself, we felt it was desirable to provide additional experimental evidence on the matter.

The most convincing evidence against the indirect route comes in fact from the displacement of 1-substituted pyrene derivatives -- ironically the same system whose reactions have caused Freund et al. (6) to invoke the indirect route. A feature of all indirect routes that commence with a radical addition is that subsequent intramolecular H-abstraction provides a set of linked aromatic systems in which the original donor framework again bears the free radical and the substrate portion has become a dihydro derivative. In other words, transfer of a single H-atom requires formation, as an intermediate, of a dihydro species. In the case of ultimate transfer of a hydrogen to the 1-position of pyrene, this intermediate would be a 1,2- or a 1,5-dihydropyrene. Both of these species are highly unstable (relative to the 4,5-dihydro species), since their formation requires destruction of the aromaticity of two of the rings of pyrene. Although there are no measured heats of formation available for these unstable dihydropyrenes, we can reliably estimate that the required intramolecular H-abstraction reactions would be more than three orders of magnitude slower for reaction of pyrene derivatives than for reaction of naphthalene derivatives (Table 1).

In contrast with these estimates, experimental results show that cleavage of pyrene derivatives is actually about two orders of magnitude faster than that of naphthalene derivatives. There is now not merely a quantitative mismatch between estimated and observed relative rates, but a qualitative inconsistency: those reactions which would have to be much slower, are actually much faster. Thus the increased susceptibility of pyrene linkages to ipso displacement that has been recently discussed (4,6) cannot be the result of a multi-step sequence of free radical reactions that has the same net result as the one-step RHT process.

CONCLUSIONS

The experimental evidence now makes it clear that cleavage induced by H-transfer is general for benzyl and alkyl linkages to aromatic ring systems. The substrate and positional selectivities of this cleavage show that it cannot simply result from displacement by free H-atoms, and relative rates in different solvent systems show it cannot result merely from reverse radical-disproportionation. Comparison of the response of coal liquefaction on the one hand and H-abstraction-- β -scission on the other to the presence of donor solvents is a strong indicator that the latter type of strong-bond cleavage, while probably important in resid conversion, does not constitute the "critical" cleavage that distinguishes between better and poorer liquefaction systems. Finally, a multi-step radical process for hydrogen transfer is ruled out by the sensitivity of linkages to the 1-position of pyrene, coupled with the marked instability of the 1,2- and 1,5-dihydropyrene intermediates that would be necessary in a multi-step process.

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TABLE 1.

Comparison of Measured Rates of Cleavage with Estimated Rates of Multi-Step Components for Naphthalene and Pyrene Derivatives.

Benzylaromatic	exptl k _{cleavage} .s ⁻¹	Estimated Rate Constants ^a for Reaction of Three-Step Intermediate, s ⁻¹		ΔH ^o Intramol H-Abs ^b kcal/mol
		Reversal	Intramol H-Abs	
1-Benzyl-naphthalene	3 × 10 ⁻⁶	5 × 10 ⁻⁸	6 × 10 ⁻⁶	~-1
1-Benzylpyrene	5.4 × 10 ⁻⁴	5 × 10 ⁻⁸	<4 × 10 ⁻³	>+14

a. Rate constants estimated according to the regimen and data sources given in reference 11.

b. Estimated by group additivity procedures as described in reference 23, and by comparison with measured heats of formation for closest available analogs, as given in reference 24.

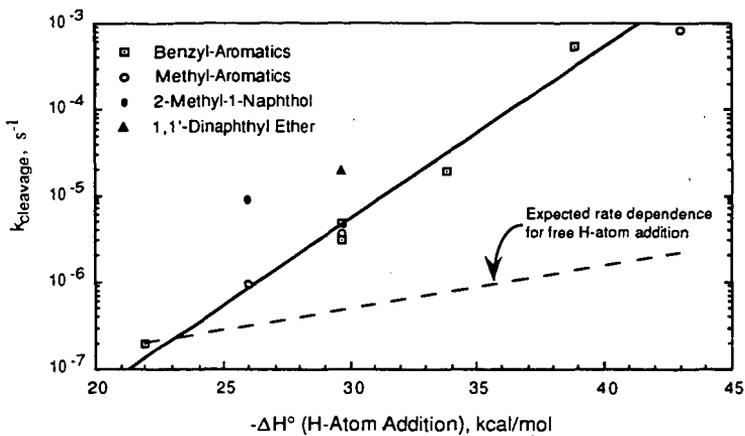


Figure 1 Measured rates of cleavage of benzyl- and methyl- aromatics in anthracene/dihydroanthracene at 400°C, as a function of the exothermicity of free H-atom addition.

Measured and estimated ΔH° (addition) are taken from reference 11. They are, in kcal/mol: phenyl, -22; 2-naphthyl, -26; 1-naphthyl, -27.9; 9-phenanthryl, -33.8; 1-pyrenyl, -38.9; and 9-anthryl, -43.