

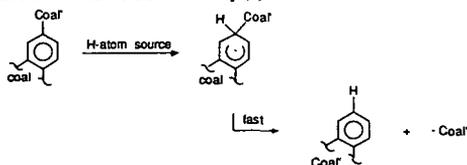
HYDROGEN-TRANSFER IN RETROGRADE REACTION -- THE HERO AND THE VILLAIN

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INTRODUCTION

Much attention has been focused over the years on the nature of the bond cleavage that takes place during coal liquefaction, pyrolysis, and combustion. Owing to the essential impossibility of determining the "critical" linkages between clusters in the organic structure of coals, much of what we now "know" has only been inferred from comparisons between coal behavior and that of model compounds or probe molecules. Nevertheless, it is now generally recognized that a picture of this bond cleavage that involves only the spontaneous thermal scission of weak bonds is, at best, incomplete and that the cleavage of strong bonds as a result of hydrogen-transfer should be included in our picture of coal conversion chemistry (1).



Scheme 1. Cleavage of strong bonds engendered by H-transfer to ipso position.

Recognition of the fact that hydrogen-transfer is a *prerequisite* to strong bond cleavage (rather than merely a subsequent step necessary to limit recombination) leads, via consideration of microscopic reversibility, to the conclusion that hydrogen-transfer is also a prerequisite to the *formation* of strong bonds, or retrograde reaction. Tracing Scheme 1 backwards, for instance, the link between Coal and Coal' is not "locked" into place until some agent removes the ipso H-atom in what amounts to the reverse of the first step. Thus, the task of increasing coal liquefaction yields may in some cases involve the dilemma that introduction of a particular H-transfer agent will increase bond *formation* as well as bond cleavage. It follows then that the relative utility of various H-transfer agents in liquefaction cannot be truly understood unless we know their proclivity for promoting both bond-cleavage and bond-formation. This paper is an attempt to assess the various categories of coupling reactions that may constitute the retrograde processes limiting coal conversion yields and their sensitivity to changing reaction conditions.

Although the importance of retrogressive reactions has become more obvious through careful studies of liquefaction kinetics and products, the fundamental chemical reactions and their kinetics have remained obscure. For instance, researchers such as Neavel recognized some time ago that soluble products could be generated *and consumed* very rapidly under coal liquefaction conditions (2). Similar observations have been made for pyridine solubles under pyrolysis conditions, where there is no added solvent (3). In a sense the whole technology of heavy oil conversion is bound up with retrograde reactions, in that thermal treatment of petroleum asphaltene under a variety of conditions can produce similar amounts of distillate, but the amount of retrograde product (coke) generated in conjunction with these volatiles is critically dependent on conditions of catalyst, medium, and hydrogen pressure (4-5). Thus the impact of retrograde processes can be quite obvious, but the detailed nature of the responsible bond forming reactions is unclear.

In order to provide a background for better addressing retrograde reactions, we have examined the literature for evidence of retrograde reactions not only in actual coal conversions, but in studies of model compounds, probe molecules, and grafted-probes, and have tried to extend our understanding of the bond-forming chemistry in some of these circumstances by mechanistic numerical modeling. This model was chemically detailed, but structurally limited -- not intended in any way to actually model the conversion of a real coal, but to ascertain how chemical factors influence certain classes of reactions under different circumstances.

This modeling incorporates the most basic of the bond cleavage types now thought to be important in coal liquefaction, and its validity is dependent of course on the appropriateness of the reactions considered. In this paper we summarize some of the results of this literature scrutiny and modeling effort.

RESULTS AND DISCUSSION

Pyrolysis of Grafted Coals. Zabransky and Stock have covalently grafted various groups to an Illinois No. 6 coal through various C-O and C-C linkages and pyrolyzed these coals using a resistively heated wire grid reactor (6-12). Through isotopic labeling of various carbons and hydrogens in the grafted groups, followed by mass spectrometric analysis of the gaseous products, identifiable portions of the grafted structures were tracked with a degree of certainty that is not achievable with unmodified coals. These studies have allowed the authors to reach a number of interesting conclusions regarding the nature of bond cleavages in structures typified by the grafted groups. Here we wish to focus instead on what limits this cleavage, specifically on how retrograde reactions compete with the bond scission processes.

Some indication of the severity of retrogression can be seen from the products reported by Zabransky and Stock (6-12) for pyrolysis of deuterium- and ^{13}C -labeled- O-n-propyl, O-n $\text{C}_{18}\text{H}_{37}$, O- $\text{CH}_2\text{CH}_2\text{Ph}$, and O- CH_2Ph Illinois No. 6 coals. Selected results are shown in Table 1, derived from their data.

The authors have discussed the extent to which the results reveal that the cleavage of strong bonds by β -scission, following either H-abstraction from an alkyl group or H-transfer to an aromatic group, are important routes for fragmentation of the grafted structures. They conclude, for instance, that the abstraction route for the aliphatic portion of alkyaromatic structures tends to be more facile than the ipso-addition route; at least when the aromatic is a single phenyl ring. These pathways account for cleavage of 2 to 40% of the grafted groups (6,9). Just as important as determination of the modes of cleavage, however, is comparison of the yields of cleaved products with the inferred yields of uncleaved, or retrograde, products. Table 1 shows the percents of the grafted portions that are converted to various cleavage products, as determined by isotopic labeling. Though the heavier products were not fully analyzed, and high precision was difficult to achieve on the scale of the experiments, the general trend is clear: substantially less than half of the grafted groups were evolved, via either weak bond thermolysis or induced scission of strong bonds, during pyrolysis to final temperatures generally in the 750 to 850°C range. This observation becomes still more striking when the rate of thermolysis of the O-C linkages in the various graftings are considered.

Table 2 shows estimated rates of cleavage for various final pyrolysis temperatures, and also the fractions of the linkage expected to be still intact by the time a particular temperature is reached (at the 1000°C/s heating rate used in the pyrolysis experiments). To take into account cage recombination, the last three columns in Table 2 are estimated by assuming that 99% of the radicals produced by thermolysis recombine before they can escape the cage, in effect extending the life of the weakly bonded species by a factor of 100 [SSD85].

The slowest homolysis is of course expected for the O-alkyl grafts, in which the O-C bonds are about 10 kcal/mol stronger than any of the O-arylmethyl cases (14). Even for this most strongly bound group, pyrolysis to a final temperature of 750°C (with zero hold-time), would leave an unconverted fraction of less than 1%, were there no recombination. However, if 99% recombination occurred in the cage, the fraction unconverted by 750°C would increase to 97%. Thus, for the O-alkyl grafted coals, the expected homolytic conversion of the graft to volatiles would critically depend on the extent of cage recombination. In contrast, the O-benzyl-type graftings have estimated homolysis rates that are higher by at least two orders of magnitude, and the fractions unconverted by 750°C would be no more than 4%, even assuming 99% cage recombination. Given this difference, it is striking that, in spite of having the slowest homolysis rates, the O-alkyl graftings are seen in Table 3-1 to have the highest fractional conversions to the corresponding alkane and its degradation products (~40%). For comparison, row 4 in Table 1 shows that only 8% of the weakly bound benzyl group of O-benzyl coal was detected as toluene. Clearly, the ease of conversion to volatile products in the case of alkyl structures is not dependent primarily on the ease of homolysis.

If the primary determinant of the extent of conversion of these weakly bound grafts is not the homolysis rate, then it must be either the rate of retrogression of these structures (including the fate of initially formed radicals), or the rate of the induced bond scission. For the case of O-nPr coal, Zabransky and Stock have shown (by examination of alkane/alkene ratios) that facile volatiles production with the O-nPr coal is not due to bond-scission induced by H-abstraction, but does indeed arise from homolysis (11,12). Thus, the conversion of O-propyl coal to aliphatic fragments is more complete than the conversion of O-benzyl coal to toluene, *in spite of* the fact that the former conversion occurs via a much slower homolysis. The successful homolysis of aliphatic linkages that are significantly stronger than the weak bond in the O-benzyl coal thus fixes the cause for the low yields of toluene on the proclivity of aromatic structures for undergoing retrograde reactions.

Pyrolysis of Polymeric Coal Models. More detail about the structural factors that facilitate retrograde reaction (other than the simple presence of aromatic groups) can be obtained from polymeric coal model studies. Several years ago, Solomon and Squire studied 27 polymers containing aromatic, hydroaromatic, and heteroaromatic groups linked together by ethylene, methylene, propylene, oxymethylene, ether, aryl-aryl, sulfide, and ester bridges (15,16), using the same heated-grid technique for the pyrolysis of the polymer models as was used by Zabransky and Stock used for their grafted coals. Because of limitations of space, we will merely summarize some of the conclusions that can be drawn from this study.

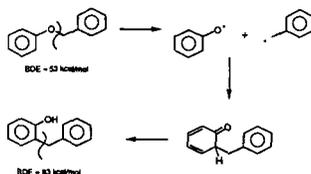
The primary focus of Solomon was on two-atom, i.e., weak linkages, for the reason that the traditional picture of thermal coal conversion chemistry then held that coal conversion resulted from spontaneous thermal cleavage (i.e., homolysis) of such weak linkages. However, precisely because most of the polymers consisted of low molecular weight clusters linked in linear chains by weak bonds, we find that the results offer a clearer view of the impact of retrograde reactions than they would with models containing some strongly linked clusters. These results reiterate some of the conclusions drawn from the grafted coal studies of Zabransky and Stock (6-12) and allow new ones to be drawn regarding the factors that limit the conversion of the polymers to volatiles. Among the most important of these conclusions are the following.

- Retrograde reactions profoundly limit volatile (or liquid) yields, which are controlled more by these coupling reactions than by the weakness of connecting bridges.
- Polymers or coal grafts containing aromatic components undergo retrograde reaction much more readily than aliphatic components.
- Increasing size of the aromatic clusters increases char yield, even under conditions where oligomer volatility limitations are unlikely to play a large role.
- As expected, the presence of hydroaromatic structure within the polymeric network decreases the retrograde reaction.
- Retrograde reactions tend to be worse for oxymethylene bridged polymers (particularly if in quinonoidal structures), notwithstanding an ~10 kcal/mol lowering of bond strength;
- Strengthening of weak ethylene bridges by removal of aliphatic hydrogen when there is no better source available contributes to char formation, but perhaps more importantly induces other crosslinking reactions to take place.

Nature of the Retrograde Reactions. From the studies highlighted above, together with related studies of coals and polymeric models and the work of Stein on the coupling of aromatics (17-21), we arrive at the following conclusions about the potential classes of retrograde reaction involving uncharged species in coal structures.

1. Radical Recombination

- Resonance stabilized radicals -- Two resonance stabilized radicals can result only in the formation of weak bonds, providing only temporary retrograde products, *except* in the case of ring recombination of phenoxy radicals. The latter case can result in successful retrograde reaction because the highly unstable initial adduct is able to rapidly rearrange through facile inter-molecular proton transfer reactions that are known (22) to be accessible to phenolic structures at coal liquefaction temperatures *even* in hydrocarbon solvents.



Scheme 2. Formation of strong retrograde linkages by ring recombination of aryloxy radicals.

- Aryl radicals -- Recombination of two aryl radicals would produce a biaryl linkage, at ca. 115 kcal/mol the strongest C-C single bond possible in hydrocarbons; however, the reactivity of aryl radicals necessarily means their concentrations will normally be far too low to participate in cross-recombination reactions, let alone self-recombination reactions.
2. Radical Addition to Unsaturated Systems
- Aryl radicals -- Aryl radicals, if formed, are known to add readily to any other aromatic system. The strength of the new bond formed means that hydrogen is readily displaced, even in the gas phase (18,21), where the primary loss process available is direct unimolecular loss of H-atoms. In the condensed phase, where H-atom loss by radical disproportionation and radical hydrogen-transfer will be relatively much more favored, we would expect aryl radical addition to be essentially irreversible. That is, during coal liquefaction effective H-atom removal would be no problem and the principal factor limiting aryl radical addition will be the rate of aryl radical generation.
 - Resonance stabilized radicals -- The addition of resonance stabilized radicals to aromatic systems constitutes the opposite extreme: the carbon-carbon bond formed will be at least 20 kcal/mol weaker than the C-H bond that needs to be displaced (13,14), i.e., direct addition-elimination or displacement of H atoms by resonance-stabilized radicals are much less favored. Such coupling requires "special" circumstance that are nonetheless present during much of the liquefaction process. These circumstances are either high concentrations of displacing radicals, the presence good leaving groups on these aromatic systems, extremely effective H-atom acceptors in the reaction mixture, or multiple opportunities for radical addition. In other words, coupling reactions of this type will be highly dependent on the nature of the H-atom removal agents.
 - Molecular coupling -- Stein found it necessary to invoke direct bimolecular coupling of closed-shell aromatics to form biradicals in order to account for the coupling of anthracene (20). This reaction can be thought of as the addition of a highly unstable biradical; no bimolecular H-transfer process is fast enough to compete with the β -scission of the resulting biradical adduct to re-generate the two closed-shell aromatics. Adducts formed by such additions can evidently be stabilized only when geometrical factors favor very rapid *intra*-molecular H-atom transfer reactions.

ASSESSMENT OF RETROGRADE REACTION BY MECHANISTIC MODELING.

In this section we summarize some results from use of a numerical reaction model (23) employing a surrogate coal structure to help address the factors controlling competing bond scission and retrograde reaction pathways during the initial stages of coal liquefaction. The addition of stabilized radicals was chosen as the retrograde reaction type, not because we believe it to necessarily be always the most important class of retrograde reaction, but because it is the class of bond-making reaction whose outcome is most likely to be sensitive to changing hydrogen-transfer conditions. The addition of resonance-stabilized radicals is highly reversible, such that if it results in successful formation of strong bonds between aromatic clusters, it will be because a very small fraction of a large number of original additions ultimately go on to stable products. For simplicity, we have limited the model to a pure hydrocarbon system, though the same general considerations will also apply to systems containing phenolics, where the presence of the -OH groups will in all likelihood further promote radical addition.

The model we have used is very detailed; it incorporates all relevant fundamental chemical reactions (non-ionic) of essentially all species, both closed shell and free radical, in the reaction system. Because of this detail, the model, of necessity, includes only a very limited set of starting structures. All models is homogeneous; it consists of relatively low molecular weight species assumed to be miscible in all proportions. We have made the simplifying assumptions that the system is free of concentration gradients and requires no mass- or heat-transport. The activity of H₂ in solution is taken to equal that provided by presumed equilibrium with the gas-phase H₂ pressure. This model was not intended in any way to actually simulate the conversion of a real coal, but to ascertain how chemical factors influence certain classes of reactions under different circumstances. There has been absolutely no attempt to force the model results to correspond to the phenomenology of coal liquefaction or pyrolysis.

Space prevents a full description of the model and results here; these details will be presented elsewhere (24). Given below is a brief summary of the results of the modeling as they apply to the prevention of retrograde

reaction. In some cases these results are a quantitative illustration of what could be qualitatively anticipated from thermochemical considerations. In other cases the results were qualitatively surprising.

- All scavengers that operate via a radical capping process have a dual role—they also act as initiators.
- "Scavengers" typically found to best aid coal conversion to volatiles or liquids appear to perform better because they are superior in some aspect other than scavenging.
- At short reaction times, where there is a large generation of fragment radicals from homolysis of the weakly bonded coal surrogate, modeling indicates that dihydroanthracene, as the better scavenger, indeed maximizes the yield of capped fragment radicals, and minimizes the yield of recombination products and radical displacement retrograde products.
- However, at long reaction times, the "better" scavenger actually *enhances* the yield of retrograde product. This is because, at longer reaction times when the burst of radicals from the decomposing coal has largely died away, the principal source of fragment radicals is abstraction of hydrogen atoms from the previously capped fragment species by the pool of scavenger radicals generated by the scavenger itself. Thus, the model elaborates a trend which has been noted previously (25), namely that coal conversion tends to be better in the presence of hydroaromatics that are *not* the best scavengers, and is evidently better because these latter scavengers tend to be better hydrogenolysis reagents, while being poorer radical initiators.
- Higher temperatures provide more reaction, but if there is not something to mitigate retrograde reactions, higher temperatures tend to cause the retrograde reactions to increase as fast or faster than the bond-cleavage reactions. This modeling result appears to be completely in accord with the common observation that increasing liquefaction temperature beyond about 440°C tends to lower coal conversion, and similarly in pyrolysis, that higher heating rates tend to decrease char yields, *primarily* when the higher heating rates are associated with more rapid removal of volatile products, (26).
- Under the conditions modeled, displacement of carbon-centered radicals from aromatic rings accounted for roughly four times as many retrograde products as did displacement of H-atoms
- The presence of H₂ does *not* inhibit retrograde product formation as much as it hydrogenolyzes retrograde products faster after they are formed. In fact, modeling indicates that H₂ can, at certain reactions times, *increase* the yield of retrograde products.
- The impact of added H₂ on hydrogenolysis (at least in the short term) does *not* come primarily through its maintenance of a useful hydroaromatic content, as has often been postulated in coal liquefaction, but through a higher steady state concentration of H• that is established long before the hydroaromatic content can be substantially affected.

Summary and Conclusions

Our examination of literature data, together with thermochemical considerations and the associated numerical modeling of simplified reaction systems leads us to the following summary picture of retrograde reaction during coal conversion.

Recombination with Phenoxy Radicals. The major case where where radical recombination can lead to a true retrograde product is ring-recombination of a phenoxy radical with resonance-stabilized carbon-centered radicals. Studies with the model compound benzyl phenyl ether have shown that the presence of scavengers can decrease but cannot easily eliminate the formation of diarylmethane linkages through this route. We suggest that facile intramolecular proton-transfer efficiently converts the initially formed and unstable keto-form to the strongly bonded phenolic form. No such isomerization pathway is available for ring-recombination of two benzylic radicals.

Dual Function of Radical Scavengers. Modeling has illustrated the apparent paradox that the best scavengers may do the worst job of preventing radical addition. Hydroaromatic structures such as 9,10-dihydroanthracene that have very weak benzylic C-H bonds will also tend to have high steady state concentrations

of the ArH• radicals generated in the scavenging act. Thus, the "better" scavengers may result in a lower steady state concentrations of candidate retrograde radicals *only* when the principal source of such radicals is something other than these abstractions, such as a rapid homolysis or β -scission. Accordingly, the concentration of resonance-stabilized radicals like benzyl and phenoxy can sometimes be decreased by scavengers, but they cannot be lowered below a minimum corresponding to the level that is generated by the hydroaromatic scavenger system functioning as an initiator.

Modeling also reveals that in many instances, the donor solvent content or H₂ pressure do not serve so much to decrease the rate of retrograde product formation as to cleave such products after they have been formed. In fact, the presence of these reagents may actually *increase* the rate of retrograde product formation at certain times. Thus, the major impact of H₂ lies not in its scavenging ability, which is very modest, but in the fact that whatever scavenging does take place produces free H-atoms, which are highly active hydrogenolysis agents. This "direct" hydrogenolysis activity of free H-atoms is seen to be a much more important effect of H₂, at least at short reaction times, than the indirect effect of maintenance of donor level.

Aryl Radical Addition. Since aryl-aryl bonds are so strong, displacement of H-atoms by addition of aryl radicals is prevented primarily by minimizing formation of these radicals in the first place. Literature results suggest the somewhat counterintuitive observation that aryl radicals are generated principally by the much larger pool of (individually much less reactive) resonance stabilized radicals.

Resonance Stabilized Radical Addition. The displacement of C-H bonds by resonance stabilized radicals (whether acyclic and therefore leading to diarylmethane linkages, or cyclic and leading ultimately to biaryl linkages) will usually be dependent not only on the concentration of potential displacing radicals, but also on the facility with which the reaction system stabilizes the intermediate adduct by removing the hydrogen atom that is being substituted. For example, modeling indicates that retrograde products from homolytically generated benzylic radicals are lower when dihydroanthracene (rather than dihydrophenanthrene) is the hydroaromatic scavenger. However, at long reaction times, when the main source of benzylic attacking radicals is the radical soup itself, the higher radical concentration provided by the "better" scavenger acts to *generate* more attacking radicals and also to more readily stabilize the adducts through radical disproportionation. In addition, the very good H-atom accepting capability of anthracene itself also increases the fraction of the initial adducts that are successfully stabilized as retrograde products.

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TABLE 1
FATE OF STRUCTURES GRAFTED TO COAL VIA PHENOLIC OXYGEN:
PYROLYSIS IN A HEATED WIRE GRID^a

Grafted Structure	% of Graft Converted to		
	C ₁ -C ₃	PhH	PhCH ₃
-nC ₃ H ₇	1.7 C ₁ 9.1 C ₂ 28 C ₃	NA	NA
-nC ₁₈ H ₃₇	7.2	NA	NA
-CH ₂ CH ₂ Ph	4.5 C ₁ ≤ 10 C ₂	≤ 1	≤ 2
-CH ₂ Ph	-	1.2	8.0
-CH ₂ PhCH ₂ CH ₃	5.3 C ₂	NR	NR
			Unaccounted ^b
			61
			≥ 83
			91

^aHeating rate approximately 1000°C/s to a maximum temperature of about 800°C

^bUnaccounted for and presumably added to the coal. Where the analysis of major fragment pieces was not reported ("NR"), this column was left blank.

TABLE 2
ESTIMATED RATES OF HOMOLYSIS AND ANTICIPATED FRACTIONAL REACTION FOR GRAFTED LINKAGES

Coal Structure	Grafted Structure	BDE ^a	k _{homolysis} (s ⁻¹) ^b				Unconverted Fraction Remaining at T ^c				Unconverted Fraction Remaining at T ^d with 99% Recombination			
			650	700	750	800	750	800	700	750	800	750	800	
CoalO-	-nC ₃ H ₇	61	8.4	4.9x10 ⁻¹	2.3x10 ²	0.65	0.09	9.9x10 ⁻⁶	1 x 10 ⁻⁵	.996	.97	.89		
CoalO-	-CH ₂ Ph	52	1.5x10 ³	6.6x10 ³	2.5x10 ⁴	0	0	0	0	0.5	0.04	5 x 10 ⁻⁶		
CoalO-	-CH ₂ - 	47	2.3 x 10 ⁴	8.7 x 10 ⁴	2.9 x 10 ⁵	0	0	0	0	1 x 10 ⁻⁵	1 x 10 ⁻¹⁹	0		

^aEstimated from values given in References 13 and 14. The assumption is made that coal structure bearing the oxygen atom is a single, unsubstituted phenyl ring. Inasmuch as this phenyl ring must have at least one other "substituent" to be a part of a polymeric coal matrix, this assumption provides an upper limit to the strength of the grafted linkage. Based on an E₀ = BDE + RT; A = 10^{13.5} s⁻¹.

^bUnreacted Fraction = e^{-(k_T t)^{0.05}}, where 0.05 is the time for the sample to heat from (T-50)°C to T_{final} at 1000°C/s, the heating rate used by Zabransky and Stock. Because k_{T-50} is a lower limit to the rate constant during the last 50°C, the calculated value over-estimates the unreacted fraction.

^dUnreacted fraction assuming 99% recombination is given by e^{-(k_{T-50} t)(0.05)(0.01)}, again an over-estimate of the unreacted fraction.