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DOE/PC/88801--T2

DE89 013676

DOE/PC/88801--T2

IMPROVED PERFORMANCE IN CO-PROCESSING THROUGH FUNDAMENTAL AND MECHANISTIC STUDIES IN HYDROGEN TRANSFER AND CATALYSIS

Received by OSTI
JUN 22 1989

QUARTERLY REPORT
FOR
CONTRACT NO. DEAC2288PC88801

DECEMBER 27, 1988 - MARCH 27, 1989

CHRISTINE W. CURTIS
JAMES A. GUIN
A. R. TARRER

CHEMICAL ENGINEERING DEPARTMENT
AUBURN UNIVERSITY
AUBURN, AL 36849-5127

MASTER

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IMPROVED PERFORMANCE IN CO-PROCESSING THROUGH FUNDAMENTAL AND MECHANISTIC STUDIES IN HYDROGEN TRANSFER AND CATALYSIS

OBJECTIVE

To gain a fundamental understanding of the role and importance of hydrogen transfer reactions in thermal and catalytic coprocessing by examining possible hydrogen donation from cycloalkane/aromatic systems and by understanding the chemistry and enhanced reactivity of hydrotreated residuum, by enriching petroleum solvent with potent new donors, nonaromatic hydroaromatics, thereby promoting hydrogen transfer reactions in coprocessing.

MAJOR TASKS AND THEIR OBJECTIVES

Task I. Elucidation of Hydrogen Transfer Reactions in Coprocessing

Objective: To attain a fundamental understanding of the hydrogen transfer reactions which occur during coprocessing and to elucidate their role and importance in achieving upgraded products.

Task II. Development of Potent Nonaromatic Hydroaromatic Hydrogen Donors for Coprocessing

Objective: To generate petroleum solvent enriched with nonaromatic hydroaromatics by metal or electrochemical reduction and to evaluate their reactivity and selectivity.

SUMMARY OF WORK PERFORMED THIS QUARTER

Literature Search

A complete literature search was performed on hydrogen donation in coprocessing and coal liquefaction. The objective of this search was to undercover the role of hydrogen transfer from different types of model molecules to one another as well as the role of hydrogen donation in coprocessing and coal liquefaction. As would be expected, the literature available in hydrogen donation in direct liquefaction is extensive. In fact over 400 papers, patents or review have been published since the early 1970's. The abstracts of these articles were carefully reviewed to ascertain the publications of primary interest to this contract.

In view of the objective of this contract in evaluating improved performance in coprocessing through fundamental and mechanistic studies through hydrogen transfer and catalysis, several areas of the literature were initially focused upon. They include (1) hydrogen transfer amongst different molecular types; (2) hydrogen transfer in coprocessing; and (3) hydrogen transfer to petroleum residue. A review of the first two topics will be presented here. The next quarterly report will delve more in depth into the first topic and will also include some aspects of the third topic.

The reasons that these topics were chosen were because of their direct implication to Task I of this contract. In Task I, we will be examining possible hydrogen transfer between cycloalkane and aromatic systems and will examine the chemistry and enhanced reactivity of hydrotreated residua. The literature provides clues as to whether such hydrogen transfer can occur in coprocessing systems.

Also included is a literature review which we previously performed which is pertinent to this study. Appendix A is a literature review which discusses the mechanisms of coal liquefaction and how these mechanisms might affect coprocessing.

Hydrogen Donation between Cycloalkanes and Coal. Clarke et al. (1984) examined the reactivity of cycloalkanes in the extraction of bituminous coal at 430°C in an inert atmosphere. Many of the cycloalkanes and aromatic systems used in this work were reacted alone at reaction conditions to test their thermal reactivity. Then they were reacted as single solvents in the presence of coal. The product activity data which were obtained from combined reactions of cycloalkanes with polynuclear aromatics of three or more rings indicated a participation in the cycloalkanes in hydrogen donation reactions. The authors (Clarke et al., 1984) claimed that cycloalkane/aromatic mixtures containing decalin/phenanthrene and decalin/pyrene yielded much higher coal extraction yields than either the cycloalkane or aromatic alone. The products obtained from the reactions showed that the cycloalkanes were converted to their hydroaromatic and aromatic analogues and, hence, some hydrogen was released from the cycloalkane. It is unclear at this point whether these molecules were totally derived from the solvent or if the reacted coal was their partial source. The authors postulated that in presence of coal derived radicals and polynuclear aromatic comprounds, cycloalkanes served as hydrogen donating species. This work has strong implications for coprocessing, suggesting that under a favorable set of reaction conditions and environment, possible hydrogen transfer may occur between the naphthenes present in the petroleum solvents and the hydrogen accepting components of the coal and the residuum.

Hydrogen transfer among model compounds was also studied by Ouchi and Makabe (1988). The compounds, biphenyl and benzyl phenyl ether, were reacted together in the presence of naphthalene, tetralin and decalin in both hydrogen and nitrogen atmospheres at temperatures of 250 to 400°C. Stabilized Ni was used as the catalyst. The primary reaction observed was direct hydrogenation of the species by H(g) on the catalyst surface.

In a thermodynamic study by Gagarin et al. (1979), the transfer of hydrogen in polynuclear systems was studied. The system used was anthracene as a hydrogen acceptor and tetralin as a hydrogen donor. Thermodynamic properties were evaluated from additivity. The key result pertinent to this review was that an excess of saturation of donor molecules hindered hydrogen transfer to aromatic systems. The calculated results agreed with liquefaction data as well as with other researchers (Curtis et al. 1981).

Schulten and Marzec (1987) examined the production of relatively low molecular weight products, 108 to 348, during the hydroliquefaction of low rank bituminous coals with decalin. The products formed belonged to seven different homologous series indicating that the weak C-O and C-C bonds in coal are composed of a variety of structures. The authors envoked the radical capping mechanism to explain the hydrogen donation of decalin.

Lang and coworkers (1984) examined the hydroliquefaction of coal under two conditions: (1) 400°C and 200 MPa with 1% $(NH_4)_2MoO_4$ and (2) 400°C and 200 MPa with decalin and $CoMo/Al_2O_3$ catalyst. Both of these conditions gave conversions of approximately 40%; however, the products achieved were different since hydroliquefaction with decalin gave coal liquids containing ~2 times less aromatic hydrocarbons than without the hydrogen donor.

Pajak and Brower (1987) have examined the mechanism of hydrogen transfer from decalin to coal. They evaluated the molar activation volume ΔV and the H/D kinetic isotope effect where ΔV for decalin at 400°C is -70 ± 5 cm^3/mol. They suggested a mechanism in which ionization of decalin accompanies or precedes the formation of the transition state. They do not believe that the rate is determined by the homolysis of the coal molecule. Other confirming evidence was that the H/D kinetic isotope effect for the coal-decalin reaction was 2.3 ± 0.2. In addition, experiments were performed with decalin in which the pressure effect and isotopic substitution effect on the rate of model reactions were also examined. On the basis of the ΔV of -55 cm^3/mol and kinetic isotope effect being 2.1 ± 0.2 for the anthracene - decalin reaction, it appears that this reaction may proceed in a fashion similar to the coal-decalin reaction.

Tagaya and coworkers (1988) have examined binary solvent systems comprised of a hydrogen donor, tetralin, and nondonor solvents to evaluate their mutual interaction during coal liquefaction and their ability to transfer hydrogen to anthracene. When combined with tetralin, the nondonor solvents fluorene, phenanthrene, indene and sulfur accelerated liquefaction; however, the pairing of n-paraffins or 1-olefins with tetralin or indene retarded liquefaction. The hydrogen donor measurement to anthracene was reflective of, though lower, than that actually observed in coal liquefaction systems.

In a recent patent application, Rudnick (1986a) examined a hydrogenation process where hydrogen was transferred from a hydrogen donor selected from greater than C_4 alkyl aliphatics and aromatics in shale oil to a hydrogen acceptor, benzophenone. A sulfur containing compound (thiophenol) or a C_2-C_{12} mercaptan was used as catalyst. Hydrogen was transferred from the shale oil to benzophenone under the conditions of 454°C for 2.5 minutes. In a related patent application, Rudnick (1986b) evaluated the conversion of alicyclic compounds into their corresponding aromatics using a sulfur containing species such as a thiol or thiophenol as a catalyst. The system evaluated included perhydropyrene as the hydrogen donor and benzophenone as the acceptor with 0.51 wt% thiophenol as the catalyst. A conversion of 94.7% benzophenone to diphenylmethane at 440°C was obtained; pyrene was observed as a product.

Interactions between hydrogen donor and aromatic systems for the liquefaction of Yallourn coal have been investigated by Chiba et al. (1987a). Hydrogen transfer by tetralin was promoted by the addition of the aromatic species fluorene or phenanthrene as manifested by increased coal conversion. The promotional effect was not observed with mixtures of tetralin with either

1-methylnaphthalene or naphthalene. Anthracene as an acceptor was used to evaluate the donor ability of the different mixtures. The hydrogen donor abilities of the different mixtures were ranked according to fluorene-tetralin>1-methylnaphthalene - tetralin > naphthalene-tetralin. Coal conversions exhibited by Yallourn coal agreed with the hydrogen donor ranking exhibited by anthracene.

Hydrogen transfer reaction may be enhanced by the presence of additional compounds as demonstrated by a study by Chiba et al. (1987b). Benzophenone and dibenzyl ether were used as hydrogen acceptors. Hydrogen transfer from tetralin was accelerated by the presence of the following compounds in the order of anthracene > fluorene > pyrene ~ triphenylmethane > phenanthrene > 1-methylnaphthalene.

In some earlier work, Clarke et al. (1983) examined the distribution of donatable hydrogen in hydrogenated anthracene oil and found that hydrogen transfer proceeded more readily in high boiling polynuclear solvents than in lower boiling single ring aromatic solvents. The amount of hydrogen transfer observed was determined by evaluating hydrogen transfer rates and coal dissolution rates in different hydrogenated oil fractions. The addition of pyrene to the lowest boiling fraction <275° improved both hydrogen transfer and coal dissolution by participating in and promoting hydrogen transfer reactions.

Coal liquefaction was examined in an indene-nondonor mixture solvent by Tagaya et al. (1988). Three different coals, two bituminous and one brown, were liquefied in pairs of solvents: indene-decalin, indene-decane and indene-tetracosane. When compared to the results of the reactions of the individual components on coal liquefaction, the indene-decalin solvent mixtures yielded conversions which were 10 to 40% higher. In addition, a synergistic effect on the production of dihydroanthracene from anthracene was also observed. The other two mixtures were detrimental to liquefaction. Hence, the indene oligomer most likely exhibited the synergistic effect by abstracting hydrogen from decalin. Hence, the role of the indene as a hydrogen donor was confirmed.

Effect of Phenolics on Hydrogen Transfer. Garry and Virk (1980) examined alcohols as possible hydrogen donors in coal liquefaction. Hydrogen transfer reactions between cyclohexanol (the donor) and anthracene and phenanthrene (the acceptors) were measured at short (0.16 hr) and long (12 hr) reaction times reactions conditions of 300 to 425°C. The initial donor/acceptor ratios of 0.125 to 15.4 to 1 were used. Three reaction pathways were observed: (1) bimolecular hydrogen donation between donor and acceptor; (2) reversion of the hydrogenated acceptor to the original acceptor by two mechanisms (a) hydrogen elimination and disportionation and (b) pyrolytic donor decomposition.

Hydrogen transfer reactions in coal liquefaction systems have been shown to be promoted by the presence of phenolics by Kamiya et al. (1978). In the liquefaction of coal the presence of phenolics compounds enhanced coal liquefaction without additional hydrogen consumption in the presence of tetralin. The efficiency of the particular phenolic was dependent on the coal used and the phenolic concentration. The mechanism by which the phenols promoted coal liquefaction was by accelerating scission of ether linkages. This mechanism was substantiated by use of a model system 2,2'-dinaphthyl which underwent decomposition under these conditions.

The effect of phenolic compounds on the dissolution of coal by aromatic-donating solutions has also been studied by Sato and Kamiya (1978). The effect of the addition of phenolic compounds on the production of SRC was studied by mixing the oxygen-containing compounds with methylnaphthalene and various additives and reacting at 435°C for 30 minutes with 20 atm of hydrogen pressure. The phenolic compounds caused hydrogen consumption to be reduced. The coal conversions are listed in Table 1.

Table 1. Coal Conversion with Oxygen Containing Compounds

Compound	Coal Conversion, %
Solvent/no additive	26.8
Tetralin	56.8
Phenylcyclohexane	41
Phenol	45.9
2-Naphthol	36.3
Cyclohexanol	89.9
o-Cyclohexylphenol	98.5
Tetrahydro-2-naphthol	99.8
Tetralin + 2-naphthol	96.0
Tetralin + phenol	98.2
Benzophenone	<26.8
Naphthoquinone	<26.8
Phenylether	<26.8

Derbyshire and Whitehurst (1981) examined the behavior of hydrogen donors, polynuclear aromatics and phenolics in actual coal liquefaction systems. They found that hydrogen donors and polynuclear aromatics act synergistically where hydrogen donors reduced charring as do polynuclear aromatics to a lesser extent. Phenolics as well as other functional compounds were associated with reactions which led to char formation.

Hydrogen Transfer in Coprocessing. Curtis and coworkers have examined hydrogen donation in coprocessing (1985, 1986, 1987a, 1987b, 1988) as well as the influence of mixed solvents on the coal conversion and the production of hexane soluble materials. Their work is summarized below. In a recent study by Curtis et al. (1987a), coal dissolution and subsequent product formation in liquefaction reactions were compared in a heavy coal-derived solvent V1067, a petroleum Maya Crude, and a Lloydminster Reduced Crude, under coprocessing conditions. In a N_2 atmosphere, 79% of the coal was converted in V1067 while Maya Crude and Lloydminster Reduced Crude yielded 28% and 13% coal conversion, respectively. In a H_2 atmosphere, all of the coal conversions increased. When a catalyst was added to each of these systems, a substantial increase in coal conversion and in the amount of pentane solubles produced was observed.

A direct comparison between the efficacy of tetralin and petroleum crudes and residua for coal conversion and production of a desirable product slate was made by Curtis et al. (1987b). These solvents were compared under three conditions: (1) a N_2 atmosphere at 400°C (2) a H_2 atmosphere at 400°C and (3) a H_2 atmosphere with a $NiMo/Al_2O_3$ catalyst at 425°C. In the N_2 atmosphere, coal conversion in tetralin was ~57%, while in the petroleum solvents, coal conversions were ~30%. In H_2, all coal conversions increased with tetralin yielding ~70% and the petroleum crudes and residua between 45 and 55%. Catalytic hydrotreatment increased coal conversions in all solvents by 10 to 15%, but the differential between tetralin and the petroleum solvents remained. The results from these experiments definitely indicated that petroleum solvents do not have the same inherent ability as a hydrogen donor such as tetralin to transfer hydrogen and dissolve coal. Therefore, either the reaction conditions need to be changed to induce hydrogen transfer from the residuum to coal or hydrogen donors need to be generated in the petroleum solvents to make them more effectual solvents for coprocessing.

Curtis et al. (1985, 1986, 1988) have further examined the role and importance of hydrogen donation reactions in coprocessing. They found that the availability of hydrogen to the coprocessing system was critical and that the hydrogen could either be present as molecular (gaseous) hydrogen or as hydrogen donors. Hydrogen donors, tetrahydroquinoline (THQ), tetralin and dihydrophenanthrene (DHP) were added to the thermal coprocessing system under both N_2 and H_2 atmospheres. The coal conversion in both N_2 and H_2 increased with increased donor concentration with THQ yielding higher conversion than tetralin and DHP yielding slightly more than THQ. In terms of pentane solubles production, THQ was a detriment particularly in N_2 while tetralin inceased the amount pentane solubles produced in reactions containing both N_2 and H_2 atmospheres. The addition of hydrogen donors depending upon their chemistry can be beneficial to either coal conversion or pentane soluble production.

Further examination of the role and importance of hydrogen donation in coprocessing was performed by Curtis and Cassell (1988a). In the thermal coprocessing of Maya TLR with Western Kentucky 9/14 coal, the addition of tetralin increased coal conversion from 48% to 70%. The influence of tetralin on the catalytic coprocessing with two different catalysts, $NiMo/Al_2O_3$ and Mo naphthenate, was also determined. When tetralin was added to the $NiMo/Al_2O_3$ coprocessing system, the combined effect of tetralin and hydrotreatment from $NiMo/Al_2O_3$ synergtically promoted coal conversion increasing yields from 69% without tetralin to 82% with tetralin. In contrast, with Mo naphthenate as the catalyst, the addition of tetralin had no effect on coal conversion or the product slate attained. With $NiMo/Al_2O_3$ substantial solvent rehydrogenation occurred while with Mo naphthenate only a small amount occurred. Based upon these results, the effectiveness of hydrogen donation in coprocessing appears to be dependent upon the reaction conditions and the activity and selectivity of the catalyst used.

Coprocessing studies performed Curtis et al. (1987a) examined six different petroleum crudes and residue, obtained from different crude sources and processing conditions as coal liquefaction solvents under three reaction conditions. These conditions were selected to determine under what conditions the coal/petroleum system would be able to convert coal and produce high quality products. In N_2, only one-third of the coal was converted and regressive reactions occurred resulting in converting some of the oil to asphaltenes. In H_2, one-half of the coal was converted to heavy products and the regressive reactions were substantially reduced. Catalytic hydrotreatment resulted in conversion of two-thirds of the coal with the production of higher quality pentane and benzene soluble products. Net oil yield increases of 6 to 13% were obtained. Within each set of conditions, only small differences were observed among the petroleum solvents' abilities to convert coal and product upgraded product; however, substantial differences were observed among the three conditions as shown by the amount of coal reacted to the different products during coprocessing. Catalytic hydrotreatment was required to convert substantial amounts of coal and to convert coal to oil.

The petroleum solvents alone were not able to convert substantial amounts of coal to preasphaltenes. Comparisons to coal-derived solvents and tetralin under the same reaction conditions showed that coal conversion was nearly doubled in these solvents. The presence of H_2 stabilized the coal/petroleum system by eliminating many of the regressive reactions and the addition of a catalyst yielded fairly higher conversions and a more highly upgraded product slate. Catalytic hydrotreatment makes coprocessing a feasible alternative for the combined upgrading of these two hydrocarbons sources.

Curtis et al. (1985) examined feasible reaction parameters for coprocessing coal with petroleum residua. A parametric evaluation showed that feasible conditions for combined processing are:

- Reaction Temperature: 425°C
- Hydrogen Pressure: above 500 psig initial hydrogen pressure
- Time: 90 minutes
- Catalyst: minimum particle size

They also observed that combined processing of coal and a petroleum solvent was sensitive to the diffusional path length of a catalyst and appeared to be more sensitive than the liquefaction of coal in a coal-derived solvent. Coal conversion and oil production from combined catalytic (powdered) processing compared favorably with that from tetralin with a powdered catalyst.

Previous work in the use of heavy oils to process coal was performed by Moschopedis et al. (1980) who used naturally occurring bitumens and heavy oils in conjunction with Alberta high volatile C bituminous coal. The reactions were performed thermally in N_2, thermally in H_2 and catalytically in H_2 using $CoMo/Al_2O_3$. The products were analyzed in terms of conversion of coal to toluene solubles. The coal conversions to toluene solubles in the coal solvation experiments using N_2 ranged from 10 to 24%, in noncatalytic hydrogenation, from 20 to 29%, and in catalytic hydrogenation, from 30 to 40%. The addition of H_2 increased coal conversion compared to an inert atmosphere; addition of a hydrodesulfurization catalyst further increased coal conversion. The toluene soluble fractions were further subdivided into asphaltenes, resins and oils. Using tetralin as a solvent, little difference was found in the conversion of coal to toluene solubles regardless of the reaction conditions. In a later work, Moschopedis et al. (1982) investigated the optimal process conditions for the coal-bitumen system. His conditions were somewhat different from those found the coal/petroleum solvent systems reported by Curtis et al. (1985).

In a study by Ricon and Angulo (1986) petroleum heavy oil mixtures as well as anthracene oil were used as hydrogen donor solvents in coal liquefaction. They observed a possible synergistic effect when the two solvents were mixed. For example, the maximum conversion temperature was lower for the mixed solvent than for either solvent alone. Rincon and Angulo claim that petroleum heavy oil acts as a hydrogen donor to anthracene oil producing hydroaromatic derivatives in the anthracene oil which in turn donate to coal. The hydrogen donors in the petroleum heavy oil were monitored as a function of temperature by ^{1}HNMR so that maximum conversion could be achieved. Rincon and coworkers (1987) have also liquefied Cerrejon coal with hydrogenated pitches at 440°C for 10, 30 and 60 minutes. Compared to hydrogenated anthracene oil, the hydrogenated pitches were better solvents because no preasphaltene production was observed.

The hydrogen donor ability of two Canadian and one Venezuelan tar-sand bitumens as evaluated by reaction with anthracene at 400°C was shown to be less than tetralin by Sato et al. (1988). When Cold Lake bitumen was combined with tetralin, the combination performed as a better hydrogen donor then tetralin. These results were confirmed by coal liquefaction reactions where the bitumen also appeared to improve the hydrogen donor quality of the recycle solvent.

In a recent study involving the coprocessing of Chinese bituminous coal, Chen et al. (1988) examined the influence of residence time, hydrogen transfer, hydrogen pressure, catalyst and temperature for Pangi coal. At 450°C, the coprocessing of Pangi bituminous coal with petroleum vacuum distillates yielded 80% distillates with low hydrogen consumption. The vacuum residue was mixed with anthracene oil in an attempt to facilitate hydrogen transfer but no positive effect could be observed. Blending of the coal with tetralin resulted in lighter products but not greater liquid yields.

Other evidence for hydrogen donation from fossil fuel sources was suggested by Vol-Epshtein and coworkers. They used a Baltic Sea kerogen concentrate as a hydrogen donor for the hydrogenation of complex phenols. Under the conditions of 400°C for 10 minutes, the kerogen was as active a hydrogen donor as tetralin.

Implications of Literature Search

Several salient points appear from the literature search on hydrogen transfer in coprocessing. Several authors (Clarke et al. 1984; Schulten and Marzec, 1987; Lang et al. 1984; Pajak and Brower, 1987) suggest that hydrogen transfer does indeed occur from cycloalkanes in the presence of coal. This evidence will be examined carefully so that any important factors which cause or influence this transfer can be incorporated into our study. Modeling these reactions without coal may be more difficult. Rudnick in his patents (1986a, 1986b) offers a very valuable suggestion that hydrogen transfer from alkyl aliphatics and aromatics in shale oil to an acceptor was catalyzed by the presence of sulfur. Of course, sulfur containing organics are prevalent species in both coal and petroleum residuum and would be present as well as perhaps influential in coprocessing. Our research involving the hydrogen transfer from cycloalkanes to aromatics will take into account these factors. The introduction of additional compound such as sulfur containing species will be considered and most likely tried so that the catalytic effects of heteroatomic species present in coal and residuum can be considered.

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APPENDIX A

Coal Liquefaction Mechanisms

Appendix A

Coal Liquefaction Mechanisms

The literature review which follows examines many of the currently held theories on the mechanisms of coal liquefaction. The most widely held theory involves thermolysis resulting in free radical formation followed by radical quenching by hydrogen usually at temperatures of 380°C and above. Evidence for and against this thermolysis radical capping mechanism is given in the discussion. The idea of achieving substantial liquefaction of coal in the presence of hydrogen donors is supported by the mechanism of solvent mediated liquefaction developed by McMillen and coworkers (1983, 1985) where bond breakage occurs at lower than thermally expected temperatures in the presence of hydrogen donors. The coal liquefaction mechanisms discussed are not mutually exclusive; several mechanisms are probably occurring simultaneously in this complicated multicomponent type dissolution process. Certain mechanisms are probably favored by different temperature regimes: thermolysis at high temperatures and solvent mediated hydrogenolysis at lower temperatures.

A recent review of several liquefaction mechanisms is given by Bockrath (1982). Apparently, the earliest coal liquefaction mechanism was introduced by Curran et al. (1967) and is initiated by the thermolytic cleavage of a single covalent bond to produce two free radical species. These free radical species are then "capped" by abstracting hydrogen from an available source, such as a hydrogen donor (hydroaromatics) compound. This thermolysis-radical-capping (TRC) mechanism may be represented as:

$$\mathrm{Coal}_1 - \mathrm{Coal}_2 \dashrightarrow \mathrm{Coal}_1^{o} + \mathrm{Coal}_2^{o}$$

$$\mathrm{Coal}_1^{o} + \mathrm{ArH}_2 \dashrightarrow \mathrm{Coal}_1\text{-H} + \mathrm{ArH}^{o}$$

$$\mathrm{Coal}_2^{o} + \mathrm{ArH}^{o} \dashrightarrow \mathrm{Coal}_2\text{-H} + \mathrm{Ar}$$

In this mechanism the ArH_2 refers to a hydroaromatic moiety with two donable hydrogen atoms and Ar is an aromatic species. The TRC mechanism seems plausible when viewed in light of coal molecular structure, which is thought to be that of polycondensed aromatic clusters connected by linkages such as methylene, ether, and sulfide groups. The major question seems to be, are these linkages broken in a purely thermolytic unimolecular process, or by some other mechanism?

The rate controlling step in the TRC mechanism is thought to be the first reaction, which is the thermal decomposition of coal into free radicals. In support of this mechanism Curran et al. (1967) cite the apparent insensitivity of the reaction to catalysts and the fact that the rate of hydrogen transfer is about the same regardless of the particular hydrogen donor molecule used, i.e., the rate controlling process is essentially thermal. A model system representing this type of behavior is the cracking of bibenzyl in various solvents as studied by Cronauer et al. (1979) and others (Livingston and Zeldes, 1981; Vernon, 1981; Stein, 1981; Mondragon et al., 1984). However, more work in the last decade seems to show that the liquefaction process is sensitive to catalysis and that different liquefaction rates or at least different products are observed in the presence of different donor species.

Since its inception, the TRC mechanism has been widely used as a model to visualize the process of coal liquefaction; however, acceptance of this mechanism as the predominant one for coal liquefaction is not universal and there appear to be certain observations which are not wholly consistent with the TRC hypothesis.

The idea of the TRC mechanism has led to a large amount of model compound work (Stein, 1981; Mondragon et al., 1984; Benjamin et al., 1978) to determine (1) which bond types in coal are weak enough to be broken by thermal energy on a coal liquefaction time scale and (2) to determine which hydrogen donor compounds are most effective in capping thermally generated free radicals. Along these lines, Bockrath et al., (1982, 1984) have studied the rate of hydrogen donation to benzyl radicals (generated from dibenzyl mercury) from a series of donors. These investigators rationalize the rates of donation from several donors on the basis of thermodynamic, steric, polarity, and other properties. It is notable that 9,10-dihydroanthracene (DHA) was about 20 times more active than 9,10-dihydrophenanthrene (DHP) in this regard, and indan was a very poor donor. Kim et al. (1982) have studied the quenching of diphenylmethyl radicals generated from pyrolysis of 1,1,2,2- tetraphenylethane. Radical concentrations during quenching were measured by ESR. It is interesting that indan (a poor coal liquefaction solvent) gave the best quenching rate in these experiments.

Using a competitive reaction of ortho-allylbenzyl radicals, Franz et al., (1983) developed a table of hydrogen donor abilities for selected solvents. It is notable that DHA was a much better donor than DHP in these experiments.

Kline and coworkers (1982, 1985, 1984) have used coupling reactions of polyaromatic species, such as 1,1-binaphthyl, o-terphenyl, dibenzophenanthrene, to study the relative effectiveness of various hydrogen donors. The exact mechanism of coupling is unclear; however, it does not proceed in absence of an hydrogen donor. One question raised by Kline's work (1984) and also by Kim's study (1982) is that indan seems to give very high activity, while being a very poor coal conversion solvent (Curtis et al. 1984). With a 1,1-binaphthyl substrate, DHP was about 5 times more active than DHA in forming the coupled product, perylene. This activity is opposite to that observed in the studies of Franz (1983) and Bockrath (1982, 1984).

The reduction of ketones, fluorenone and benzophenone, also has been used to evaluate the relative efficiency of donor solvents (Later and Camaioni, 1985). The proposed mechanism is complex and involves a number of radical reactions. It is notable that the initial reaction is bimolecular and involves the donor molecule, rather than simple unimolecular thermolytic cleavage as depicted by the TRC mechanism.

The popularity of the TRC mechanism may be in part due to its simplicity. The rate controlling step in TRC is thermolysis of a single molecule, as other proposed mechanisms appear more complex and contain additional steps. In spite of its popularity, some criticisms have been noted against the TRC mechanisms. Several of these are given by Brower (1982). According to Brower (1982) and Stein (1981), an examination of model compound literature pertaining to coal reactions, shows that relatively few bonds are capable of being thermolytically cleaved at coal liquefaction temperatures and time scales. For example, the half-life of dibenzyl at 673 K is on the order of 10 hours (Cronauer, 1979). Thus, there do not seem to be enough weak bond types in coal to obtain the degree of liquefaction achieved at normal processing conditions by thermolysis alone. It is known, however, that certain bond types can be made more susceptible to thermolysis by substituent groups, such as hydroxyls (-OH), which coal is known to contain (Benjamin et al., 1978; McMillen et al., 1981). It is also known that the thermolysis rates of diaryl ether, are increased with the number of polycyclic rings in the aryl structures (Kamiya et al., 1983; Benjamin et al., 1978). This increase in reactivity could be an important factor in coal liquefaction where three and four ring structures are common. Brower (1982) also argues against the TRC mechanism on the basis of an isotope effect; the reaction rate of deuterated versus protonated tetralin with coal is different. Since the TRC mechanism would show no isotope effect, the presence of this effect mitigates against a simple TRC mechanism with thermolysis as the rate controlling step. Other criticisms of the TRC mechanism are also presented by Brower (1982).

Finseth et al., (1983) using D_2 gas in coal liquefaction experiments has observed that D is incorporated into many positions, not just the alpha-position, implying a mechanism other than simple thermal cleavage and radical capping.

In coal solvolysis experiments, Curtis et al. (1984) have shown DHP to give better conversion than DHA, although the effect is dependent on the donor concentration. However, according to McMillen et al. (1983) the ArH-H bonds in DHP are at least 6 kcal/mole stronger than in DHA suggesting that if the TRC mechanism is operative, then DHA should be the more effective solvent (Billmers et al., 1985). As noted earlier, Bockrath et al. (1984) has shown DHA to be more effective for capping benzyl radicals and Kline and Harrison (1982) found DHA to be more effective than DHP for producing a coupling product, perylene. The decomposition rate of diaryl ethers was found to be very dependent on the particular hydrogen donor used and its concentration, with DHA being most effective (Kamiya et al., 1983). In addition, sometimes, purely aromatic compounds, like pyrene, are also particularly effective for coal conversion, even in the absence of H_2 (McMillen et al., 1983). The above investigations suggest that there is no clear correlation between coal solvolysis and rates of hydrogen donation to thermally created free radicals and imply that mechanisms other than simple TRC are operative.

Other free-radical mechanisms than TRC have been proposed for coal liquefaction and presently appear to be gaining some acceptance. The major difference in these alternative radical mechanisms is the step in which the coal bonds are broken, which generally involves a radical attack, rather than simple homolysis. For example, King and Stock (1982) have shown that phenols can enhance the cleavage of certain C-O and C-N bonds, whereas thermolysis alone is ineffective. Kamiya et al., (1983) have also shown that different hydrogen donors enhance bond cleavage rates.

In a series of papers, McMillen and coworkers (1980, 1985) have postulated a mechanism termed solvent promoted or solvent mediated hydrogenolysis (SMH), as an alternative to the TRC mechanism. The SMH mechanism is based on the fact (also noted by others) that very strong model compound bonds can be broken on coal liquefaction time scales at 673K in the presence of appropriate donors (such as DHA, DHP). No reaction is observed in the absence of the donors; hence, simple thermolysis is not operative. The proposed mechanism involves attack of coal bonds by solvent radicals, ArH^o, as given below:

$$\text{Coal-Coal} + ArH^o \text{ ----> } Ar + \text{Coal-H} + \text{Coal}^o$$

$$\text{Coal-Coal} + ArH^o \text{ ----> } \text{Coal-ArH} + \text{Coal}^o$$

The process whereby Ar (aromatic) species shuttle H^o to cleavable coal bonds, is sometimes referred to as hydrogen shuttling. It is not necessary to form a stable hydroaromatic for this process to occur. The SMH mechanism is initiated by a bimolecular process, rather than unimolecular thermolysis as in the TRC mechanism. The solvent radicals necessary for the SMH process can be readily formed in coal liquefaction systems by solvent molecular disproportionation as below:

$$ArH_2 + Ar \text{ ----> } 2\ ArH^o$$

Stein and coworkers (1981) have given some discussion on the relative reactivity of the DHA versus the DHP donor systems; however, it is not clear which system would give the best coal conversion, due to competing effects involving radical stability and radical initiation steps.

The preceding review has several implications in understanding the fundamental hydrogen transfer reactions occurring in coprocessing. Petroleum has many of the same compound types as exist in coal liquids, e.g., paraffins, aromatics, naphthenes, but they are present in much different proportions, e.g., petroleum has more paraffins and naphthenes while coal liquids have more aromatics. This difference means that the same mechanisms discussed above with reference to coal dissolution in liquefaction may be applicable, to a greater or lesser degree, in coprocessing.

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