MASTER

A GENERAL QUANTITATIVE MODEL FOR COAL LIQUEFACTION KINETICS: THE THERMAL CLEAVAGE/HYDROGEN DONOR CAPPING MECHANISM*

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Abstract

A mechanism for coal liquefaction, based on the concept of thermal cleavage-hydrogen capping donor complexes, is proposed and the quantitative agreement between the derived rate laws and the kinetic data obtained from fifteen publications is presented. The mechanism provides rate laws which describe the preasphaltene, asphaltene, oil and gas time/yield curves for the coal liquefaction process. A simplistic dissolution model is presented and used to relate the proposed mechanism to the experimentally observed products. For the diverse coal liquefaction systems studied, the rate constants obtained from analysis of the benzene solubles plus gas/time data vary from ~ 1 to $46 \times 10^{-3} \text{ min}^{-1}$ for data covering the later stages of conversion at temperatures between 350° to 450°C . The rate constant ranges for preasphaltene, asphaltene, oil and gas formations were found to be 1.0 to 56.0 min^{-1} , 0.03 to 0.1 min^{-1} , 0.003 to 0.1 min^{-1} and 0.007 to 0.2 min^{-1} respectively over the 350° to 450°C range. The rate constant ranges for preasphaltene and asphaltene disappearance were found to be 0.03 to 0.09 min^{-1} and 0.005 to 0.06 min^{-1} respectively. Based on the quality of the mechanistic fit to the reported coal liquefaction systems, which cover a diverse range of reaction conditions, coal types and donor solvent compositions, it is proposed that the donor solvent/thermal bond cleavage/hydrogen capping mechanism provides a good, quantitative description of the rate limiting processes. Interpretation of the rate constant/temperature dependencies in terms of transition state theory indicates formation of the activated complex can involve either physically or chemically controlled steps. A uniform free energy of activation of 52 kcal was found for the diverse liquefaction systems indicating a common transition state describes the reactions. Thus the proposed mechanism unifies the diverse liquefaction kinetic data by using a set of

uniform reaction sequences, which have a common transition state, to describe the conversion chemistry. The mechanism thereby creates a common base for inter-comparison, interpretation and evaluation of coal conversion for the broad range of processes currently being investigated in the liquefaction field.

Introduction

As a result of numerous studies reported in the literature on the kinetics of coal liquefaction, a growing insight into the kinetic processes and the general nature of the key chemical stages responsible for product formation is emerging. The kinetic processes referred to here are the reported time dependencies of the dissolution of the coal into preasphaltene, asphaltene, oil and gaseous products. The nature of the chemical steps has evolved in the literature towards the generalized concept that the rate limiting reactions involve thermal cleavage and hydrogen capping of key bonds in the organic matrices comprising coal and coal products. Work at this laboratory on the basic kinetics and mechanism of hydrogen transfer by donor solvents has resulted in a general mechanism for the donor solvent chemistry. The purpose of the present paper is to propose a general quantitative mechanism based on the thermal cleavage/hydrogen capping concept incorporated into the donor solvent mechanism and show how it agrees with the coal liquefaction kinetic data published in the literature.

The Coal Liquefaction Process

The chemical process of converting coal to soluble fragments using donor solvent systems has been extensively studied and numerous reaction sequences have been proposed. The diversified interpretations of the kinetic data by the original investigators ranges from applying simple (e.g. zero, first and second order) rate laws¹⁻²⁹ through complex free radical mechanisms³⁰⁻³³ to polynomial curve fitting.³⁴ The purpose of the present reanalysis of the published data is to present a single mechanism which can be applied to all of the published data.

The dissolution of coal produces a range of products commonly grouped in the following classes based on solubilities: preasphaltenes(P), asphaltenes(A), oils(L) and gases(G). Thus coal can be conceptualized as being clusters of chemically bonded organic systems composed of P, A, L and G species as depicted in figure 1-a. The chemically controlled processes involve the competing of hydrogenative capping with carbonization/polymerization reactions for the free radicals resulting from thermal bond cleavages. The extent of coal conversion to a given product class based on solubilities is thus a measure of the degree of competition between these reactions. The cleavage/capping reactions yield products which are soluble in less polar solvents than the reactants due to decreased molecular weight and/or loss of polar functional groups. The carbonization/polymerization reactions lead to products of lower solubility than the reactants or insolubility due to formation of material of higher molecular weight than the starting material.

A large fraction of the coal liquefaction studies lump the asphaltene, oil and gas yield together by reporting the kinetic data as benzene solubles plus gas. Inspection of the resulting coal liquefaction kinetic data reveals that the reported benzene soluble plus gas product yields vs. time plots have a com-

mon curvature (see figure 1-b) which is strikingly similar for the diverse coal/donor solvent systems studied. That is, despite the fact that these systems vary markedly in chemical composition due to coal heterogeneity and donor solvent composition, a characteristic dissolution-time behavior exists. Thus, it is possible that a common reaction mechanism might describe the reported coal kinetic data.

The extent to which hydrogenation of unsaturated bonds results in transfer of organics between product classes is currently unknown and is therefore treated implicitly in the model. The model does not include reactions for the formation of products of higher molecular weight than the reactant or insoluble residues resulting from carbonization and polymerization (e.g., formation of preasphaltene from polymerization of asphaltenes) processes. The thermal cleavage of bonds yields free radicals and will result in repolymerization and/or carbon forming reactions if the hydrogen for capping is not available. The model outlined in Figure 1 assumes the liquefaction process is run under conditions such that these reactions represent minor reaction pathways.

The following liquefaction model, depicted in figure 1-a, is based on the reported conversion/product sequences reported in the literature.^{4-9,13,17,24,28,29,38,50} The preasphaltenes are those organics which are soluble in pyridine but insoluble in benzene. The P_f preasphaltene products (see Figure 1-a) are formed from thermal cleavage and hydrogen capping of the most highly labile bonds in coal as evidenced by their rapid formation. Depending upon the type of coal, the P_f products will undergo further conversion to varying extents. Those preasphaltenes which are converted P_c will yield A, L, G and/or additional P products and therefore are conceptualized in Figure 1-a as bonded clusters of the four product classes. The asphaltenes (benzene

soluble but hexane insoluble) formed during coal liquefaction A_f are analogously thought of in terms of A, L, and G bonded clusters. Those asphaltenes which undergo further conversion by the cleavage/capping process (A_c of Figure 1-a) yield L, G and/or additional A products. As shown in Figure 1-a, the oils (hexane soluble) and gases formed during liquefaction are taken as stable products with respect to further conversion.

This simplistic view of coal liquefaction will be used to explain the proposed thermal capping mechanism. The identity of the chemical composition of the molecules in the four product classes or of the ten possible types of configurations between classes is not required to derive the mechanism. Note, however, that the rate constants for cleavage of the different types of chemical linkages, grouped according to solubilities, will result from the application of the mechanism to the literature data.

The Thermal Cleavage/Hydrogen Donor Capping Mechanism

A commonly proposed qualitative interpretation of the sequence of events which lead to coal liquefaction is the following: thermal cleavage of key bonds in the coal and coal products resulting in free radical species which are subsequently stabilized by donor species capping the radical sites with hydrogen. The thermal cleavage/hydrogenative capping sequence progresses with time to yield the desired lower molecular weight products with enhanced hydrogen-to-carbon ratios.

Evidence supporting the concept of thermal bond cleavage as the rate limiting reaction in coal liquefaction has been based on correlations between the physical behavior of coal and the dissolution of coal as functions of temperature. The temperature range over which coal plasticity occurs has been reported to correlate with the thermal decomposition of that coal.^{1,3} The bulk of

swelling and changes in thermal behavior for coals occurs in the 350-450°C range which is also the temperature range for coal liquefaction processes.³⁸ The results of viscosity, calorimetric and thermo-solvolytic studies on coal over the 250-500°C range showed that marked changes in these physical parameters occurred in the 350 to 450°C liquefaction range. This data has been interpreted in terms of thermal cleavage of bonds.³⁹ A new approach, based on heating coal in the presence of radical scavengers, has been reported to show that free radicals are produced during coal hydrogenation.³² The H₂ yields from heating coal at 400°C in the presence of the radical scavenger benzoquinone were found to be 5 times greater than when no scavenger was present. The increased H₂ yield was attributed to the benzoquinone stabilizing free radicals which normally would have consumed H₂ to achieve stabilization. A recent ESR study on the generation of free radicals during pyrolysis of fluids reports the onset of radical formation in the 400 to 500°C range for compounds of interest to coal liquefaction (i.e., bibenzyl, tetralin, indene).⁴⁰

The particular form of the cleavage donor capping (CDC) mechanism proposed here is based on kinetic studies of donor solvent systems^{35,36,37} (particularly the tetralin system). These investigations showed that the molecules comprising the donor solvent systems exchanged hydrogen via a heterogeneous process with the rate-limiting reaction involving hydrogenated/dehydrogenated paired complexes. Thus, for the tetralin (T), 1,2-dihydronaphthalene(D), naphthalene(N) system, the mechanism involves the following rate-limiting reactions

where the slant (/) denotes complexing of the organic molecule with dehydrogenated S_n or hydrogenated $(S/H)_n$ catalytic surface sites. The rate laws derived from this mechanism were found to fit the kinetic data quite well³⁷ as shown in Figure 1-c. The key points of this donor solvent mechanism, relevant to the CDC mechanism, are the assignment of the rate limiting steps to the oxidation/reduction reactions occurring within the organic molecule/hydrogen donor site complexes and the imposing of a time dependence on the populations of these complexes in the kinetic treatment. In the CDC mechanism, these same assignments will be invoked with the minor adjustment of generalizing the definition of the hydrogen donor site component of the complex to include either heterogeneous (i.e., catalytic surface) or homogeneous (i.e., donor solvent) species. A similarity in curvature for the typical coal product behavior and the donor solvent data becomes evident when one reviews the literature. For example, the literature oil and gas curves^{7-9,17,59} parallel the initial naphthalene formation behavior and the preasphaltene curves^{7-9,17,39,59} correlate with the 1,2-dihydronaphthalene. These similarities in kinetic behavior suggest that a mechanism paralleling the donor solvent model might be applicable to the coal data.

Interpretations of liquefaction results have invoked the concept of direct interaction between a donor solvent and the reactive coal site. Since the internal surface area of coal is greater than the external area it has been argued that most of the chemistry occurs within the coal with the rate of dissolution being dependent upon the concentration of unreacted solvent at the reactive

sites.² The observed two-fold increase in the preasphaltene liquefaction yield for a coal/donor solvent system compared to the coal/H₂ system has been cited as evidence for the importance of the availability of donor solvent hydrogen during the early stages of liquefaction.⁴¹ This same study furthermore supports the idea of chemical processes occurring inside the coal particles as evidenced by the presence of a significant portion of the products remaining within the coal particles in the initial stages of liquefaction. Based on particle dissolution results it has been argued that hydrogen transfer is a required prerequisite as evidenced by the fact that the rate of particle disintegration increases as solvent hydrogen donating activity is increased.⁴² The fact that poor donor solvents result in increased semi-coke yields further demonstrates the importance of the donor solvent/reactive site interaction.³⁹ Larger yields have been observed from coal/donor solvent systems as compared to coal/H₂/catalysts systems reacted under identical conditions³ (or equivalently the higher temperatures required for the coal/H₂/catalyst system to achieve comparable conversion levels). These observations suggest that the donor solvent is not just donating hydrogen but may also be influencing the energy required for bond cleavage via complexation.

The importance of the direct complexing between a coal type bond cleavage site and a hydrogen donating molecule is most clearly demonstrated by two quite different studies.^{20,40} The softening temperature of a coal briquette is lower when the hydroaromatic 9,10-dihydroanthracene is present in the briquette as compared to the undoped coal briquette or briquette doped with an equivalent amount of anthracene.²⁰ If one accepts the argument that the softening temperature is a measure of the onset of thermal bond cleavage, these briquette results can be

interpreted as evidence for the lowering of the onset of thermal bond cleavage in the hydroaromatic system due to complexing of the thermal cleavage sites by 9,10-dihydroanthracene. The clearest, direct evidence of the temperature lowering of thermal bond cleavage by hydroaromatics comes from a recent ESR study on thermal free radical formation.⁴⁰ These investigators reported that indene in tetralin formed comparable indenyl radical concentrations at temperatures 60°C lower than a corresponding benzene solution (e.g., 400°C vs 460°C).

Based on the above results and the constraints found to apply to the donor solvent systems,^{36,37} the CDC mechanism treats the organic species (R-R) to be thermally cleaved as being the solvent cage complex (R-R/(H)_n) where (H)_n is the donor solvent cage composed of hydrogen rich species (H). The R-R/(H)_n complex undergoes the rate-limiting free radical formation reaction*

Reaction 1 is immediately followed by the faster hydrogen capping reaction

*Note that the replacement of reaction 1 with the thermal bond cleavage step

where complexing with a hydrogen rich species is not invoked, will yield equivalent analytical equations for the P, A, L and G time dependencies if it is assumed that the diffusion apart of the R· species is an efficient, rapid process. However, in view of the experimental results cited above and in the liquefaction transition state section which indicate complexing is important to the cleavage step, the present treatment will be based on the form of reaction 1 involving complexing since it is most consistent with the current understanding of the bond cleavage step. Clearly further experimental work on this point is needed before the matter can be resolved.

which yields lower molecular weight products with enhanced hydrogen-to-carbon ratios. The breakup of the product complexes

are taken to be rapid reactions with respect to Reaction 1. This general reaction sequence applies to formation of any of the four product classes (i.e., P, A, L, G).

The differential rate law for Reaction 1 is

$$\frac{-d(\overset{\cdot}{R}-R/(H)_n)}{dt} = k_i (\overset{\cdot}{R}-R/(H)_n)$$

which, upon integration, is simply

$$(\overset{\cdot}{R}-R/(H)_n) = (\overset{\cdot}{R}-R/(H)_n)_0 e^{-k_i t} \quad (1)$$

where k_i is the rate constant for thermal cleavage of a given R-R bond and the $(\overset{\cdot}{R}-R/(H)_n)_0$ term is the total concentration of $\overset{\cdot}{R}-R/(H)_n$ which is formed in attaining complete reaction. For the depolymerization of a given product class, for example, for the formation of gases G from the asphalthenes, the rate of formation will be equal to the corresponding rate of complex cleavage:

$$\frac{dG}{dt} = - \frac{d(R-G/(H)_n)}{dt} = k_{fg} (R-G/(H)_n) \quad (2)$$

where R-G denotes a bond group, see Figure 1-a, which will yield a gaseous

product (i.e., the $(R-G/(H)_n)$ term is equivalent to the $(R-R/(H)_n)$ term of equation 1). Substituting the equivalent of equation 1 into 2 and integrating yields

$$G = G_{fo} (1 - e^{-k_{fg} t}) \quad (3)$$

where k_{fg} denotes a "generalized" rate constant for formation of gaseous products and the G_{fo} term is the total concentration of gases formed when the reaction is run to completion (i.e., equivalent to the $(R-R/(H)_n)_0$ term of equation 1). Figure 1-d shows the characteristic plots obtained using equation 3.

For the preasphaltene class P, as discussed above, cleavage of coal bonds (see figure 1-a) will result in the formation of preasphaltenes P_f and some fraction of these preasphaltenes P_d will undergo further conversion. The differential rate law for P formation will therefore involve the difference between the rates of cleavage for P_f formation and P_c loss

$$\frac{dP}{dt} = \frac{d(P_f/(H)_n)}{dt} - \frac{d(P_c/(H)_n)}{dt}$$

or

$$\frac{dP}{dt} = k_{fp} (P_f/(H)_n) - k_{cp} (P_c/(H)_n) \quad (4)$$

Substituting Eq. 1 into 4 and integrating

$$P = P_{fo} (1 - e^{-k_{fp}t}) - P_{co} (1 - e^{-k_{cp}t}) \quad (5)$$

where P_{fo} is the total concentration of preasphaltene formed during the reaction. The P_{co} term is the total concentration of preasphaltene converted to nonpreasphaltene product during the reaction. The k_{fp} and k_{cp} are the corresponding generalized rate constants. Similar arguments and definitions apply to the asphaltene class such that the differential rate law is

$$\frac{dA}{dt} = \frac{d(A_f/(H)_n)}{dt} - \frac{d(A_c/(H)_n)}{dt}$$

or

$$\frac{dA}{dt} = k_{fa}(A_f/(H)_n) - k_{ca}(A_c/(H)_n)$$

which integrates to

$$A = A_{fo} (1 - e^{-k_{fa}t}) - A_{co} (1 - e^{-k_{ca}t}) \quad (6)$$

Figure 1-e and 1-f show the characteristic plots obtained using equation 5 and 6 respectively.

For the oil products the published yield/time data indicate that, once formed, the oil does not react further under normal liquefaction conditions. Thus, as with the gaseous products, there is only formation of product

$$\frac{dL}{dt} = - \frac{d(L_f/(H)_n)}{dt} = k_{fl}(L_f/(H)_n)$$

and the resulting integrated rate law is

$$L = L_{fo} (1 - e^{-k_{fl} t}) \quad (7)$$

Figure 1-d shows the characteristic plots obtained using equation 7.

The defining of the product k 's as "generalized" rate constants is based on the results obtained in the present study which shows that one is able to fit the literature kinetic data with Eqs. (3), (5), (6), and (7). The formation of a given product class might be expected to involve cleavage of bonds having a range of reactivities and, therefore, different rate constants. That is, taking the formation of gas as an example, the form of equation (3) would be

$$G = \sum_i G_{fo}^i (1 - e^{-k_{fg}^i t})$$

where the yield of gas is the sum of i terms due to cleavage of i bonds having different rate constants k_{fg}^i . However, since one can fit the existing data with single k_g functions, there is no need to impose multiple terms. If the previously discussed complexing of the organic R-R sites is strongly influenced by the $(H)_n$ species (e.g., the donor solvents) such that the activation energy for reaction approaches a common value for the bonds having different reactivities, a leveling in chemical reactivity would result for a given product class. Such a leveling of reactivity provides an explanation for single rate constant terms being sufficient to describe the kinetics for a given product class.

Numerous experimental observations have been interpreted as evidence of the heterogeneous nature of the coal liquefaction mechanism. Coal pyrolysis in

the absence of catalysts gives comparable yields in the presence or absence of H_2 .^{1,3,41} The temperature dependence of coal particle dissolution has been reported to behave in a manner consistent with a high energy of activation. This result has been interpreted as evidence that the rate controlling process involves surface chemical reactions.⁴² Minerals have been reported to catalyze coal liquefaction and donor solvent hydrogenation.^{16,19,32,43-47} The hydrogenation/dehydro catalytic activity of minerals common to coal has been demonstrated for the tetralin donor solvent system.⁴⁸ Thus the coal particle dissolution and spent donor solvent rehydrogenation mechanisms involve heterogeneous reaction. The CDC mechanism accounts for these heterogeneous reactions since in these systems the hydrogen rich species $(H)_n$ would involve catalytic surface sites. For example,³⁷ as previously discussed, the hydrogenation/dehydrogenation of the tetralin donor solvent system involves catalytic surface sites S_n and $(S/H)_n$. Because coal liquefaction is known to be catalyzed by inherent minerals, as well as by added catalysis, it seems reasonable to imply that at least part of the $(H)_n$ species involve heterogeneous sites. The model thus points out an area of uncertainty: the relative importance of heterogeneous (eg., complexing with catalytic surfaces) vs. homogeneous (eg., complexing with hydrogen donating organics) cleaving/capping reactions.

Frequently, the kinetic data in the literature reports product yields as total benzene solubles plus gases (B). In terms of the asphaltene, oil and gas products

$$B = A + L + G \quad (8)$$

One can substitute equations (3), (6), and (7) into this relationship to obtain

the time dependence of B. If asphaltene conversion is the sole source of gas and oil, a condition very likely in the latter stages of conversion, one finds equation 8 reduces to

$$B = A_{fo} (1 - e^{-k_{fa}t}) \quad (9)$$

since

$$L + G = A_{co} (1 - e^{-k_{ca}t})$$

Equation 9 will apply to the majority of the studies on benzene solubles because they tend to cover only the latter coal conversion stages. For those studies where the conversion of coal to benzene solubles extends into the earlier stages of conversion, the formation of A, L and G will have a fast component due to the rapid conversion of the coal and preasphaltene. Thus one might expect the equation

$$B = B_{fo} (1 - e^{-k_{fb}t}) + A_{fo} (1 - e^{-k_{fa}t}) \quad (10)$$

to describe the kinetic data where the B_{fo} term is the total concentration of rapidly formed product. Thus equation (8) reduces to equation (9) if the loss of asphaltene is responsible for the total yield of oil and gas (that is, the negative term in equation (6) is equal to the sum of equations (3) and (7)). The failure of equation (9) to fit the data is taken as evidence for the formation of significant quantities of oil and/or gas directly from the coal and/or preasphaltenes, a process most likely in the early stages of conversion.

Indeed, when equation (9) does fail, it is with data that covers the initial conversion period and equation (10) is found to quantitatively fit the total benzene or total pyridine solubility data. The two term form of equation (10) parallels the mechanisms in the literature which treated liquefaction as involving a combination of fast and slow reactions.^{10,11,23-25,28,29}

During the initial stages of coal conversion, the consumption of hydrogen, external to the coal (i.e., donor solvent hydrogen or H_2), is negligible while for the coal the hydrogen content decreases and the aromatic content increases.^{10,11,15,18,4} Heating of a HVCB coal at 400°C using a non-donor solvent was found to yielded 25-30% conversion to low molecular weight product.⁴⁹ The addition of a radical scavenger to coal reacting at 400°C under a nitrogen atmosphere results in a five fold increase in the H_2 yield.³² All of these results have been cited by the original authors as evidence for the presence of autogeneous hydrogen which is utilized in the initial stages of coal conversion to stabilize the free radicals produced by thermal cleavage. The CDC mechanism proposed here is consistant with the concept of autogeneous hydrogenation and is interpreted as evidence for the pre-existence of complexed $(R-R/CH)_n$ sites. Some of the initial conversion yields might also include the release of physically trapped products. Additional data on the early stages of conversion are required before the validity of these explanations can be tested further.

Quantitative Fit

The majority of the reported kinetic data on liquefaction of coal using donor solvents typically cover only the last ~ 50% or less of the total coal conversion process. Furthermore, the majority of the data are reported as benzene solubles plus gas. However, these studies do yield information of value in determining the mechanism of coal liquefaction. Table 1 contains the rate con-

stants obtained using equation (9), the conversion ranges covered in the original work and related information for these studies. Figures 2 to 8 show the reported data and resultant calculated fit for equation (9) in its linearized form:

$$-\ln X = k_{fa} t \quad (11)$$

where

$$X = \frac{A_{fo} - B}{A_{fo}}$$

It should be noted that generally only those studies which reported four or more statistically distinct kinetic points were considered in the present study. As indicated in Table 1 by *, the majority of these studies did not report a value for complete conversion A_{fo} . Therefore a value was estimated based on the existing data. The limited validity of the assumption that one can treat asphaltene conversion as the source of oil and gas formation is evident from the systematic curvature present in several of the benzene solubility data plots (for example 2g, 6a, 8c). Due to the data scatter and limited conversion ranges covered, attempts to treat such data in terms of equation 10 were unsuccessful. Considering the experimental difficulties in obtaining reproducible data and the complex chemistry of these coal conversion systems, the correlation of these benzene solubility data by equation 11 is, in general, quite reasonable.

The results from these benzene solubility studies show that for the twenty different liquefaction systems studied, the rate constants fell within the 1 to $46 \times 10^{-3} \text{ min}^{-1}$ range. This rate constant range pertains to the latter stages of the liquefaction process and temperatures between 350 and 450°C as indicated in Table 1. The fact that these diverse coal/solvent systems yield a relatively

small rate constant range supports the concept of a common mechanism for coal liquefaction.

To the extent that the coal conversion ranges are comparable for a given coal study, one can discuss trends and correlations on a relative basis. Hill's 2-a, 2-b, 2-c, and 2-e data cover very roughly the same conversion range and the resultant Arrhenius plot and parameters are shown in figure 9a. Similarly, Hill's two stage extraction data, 3-b, 3-c and 3-d are for comparable ranges and the corresponding Arrhenius treatment is shown in figure 9a. Storch's comparable ranges for the uncatalyzed (6-a and 6-b) and SnS catalyzed (6-c, 6-d and 6-e) liquefaction studies yield the Arrhenius plots shown in figure 9b. Within the limited validity of this treatment of Storch's data, the SnS catalysts lowers the activation energy by a factor of ~ 1.5 . The Arrhenius plots for the rate constants from Guin's (figures 5-f and 5-g) and Curran's data (figures 4-g and 4-h) are shown in Figure 9a while those from Guns's (6-f,g,h; 7-a,b,c,d) and Liebenburg's (7-e,f,g,h; 8) data are shown in Figure 9c. For the 180 bar data of Liebenburg, the 440°C rate constant was excluded on the statistical grounds that the value falls outside the 90% confidence interval defined by the remaining rate constants. Inspection of the corresponding conversion/time plot in the original paper shows this 440°C data has a markedly faster conversion rate. Thus the data and resultant rate constant pertain to a conversion range dissimilar to the majority and cannot therefore be utilized in intercomparisons.

Analysis of Guin's data on the influence of coal pretreatment (figure 7-c, 7-d and 7-e) show that water washing has little if any effect on the rate constant calculated in the present study. However the demineralized coal k_{fb} is approximately half the untreated value.

Of the seven different coals studied by Neavel, the data for one coal, the high-volatile C bituminous (coal d in Neavel's table 1), covered 95% of the total conversion to benzene solubles plus gas. The other six coals were studied over limited ranges and, therefore, were treated using equation 11. Table 1 and Figures 5-a through 5-f show the resulting rate constants and fits for these six coals. The benzene solubility data for the seventh coal, Neavel's coal d, are shown in figure 10-a along with the calculated fit using equation (10). The fitting of equation 10 to Neavel's and to Whitehurst's data on the total pyridine soluble product are shown in Figures 10-b and 10-c respectively. Analogous treatment of three of Storch's data sets, previously approximated using equation 11 (Figures 6a, c and d), are shown in Figures 10-d, e and f. Attempts to treat Storch's data corresponding to Figures 6-b and e were unsuccessful indicating these data bases are not sufficient to warrant the dual term treatment of equation 10. The relevant rate parameters and ranges for these studies are given in Table 2. The Arrhenius plots for the full range analysis of Storch's data are shown in Figure 9c. Equation 10 describes these systems quite well and indicates the liquefaction of coal, when studied over the major portion of the conversion range, proceeds via initially fast reaction sequences followed by slower, by factors of $\sqrt{10}$ to 100, reactions.

The applicability of equation 5 and 6 to the reported complex product kinetic behaviors is demonstrated for the preasphaltenes and asphaltene data in Figures 10-g through j. The quality of the fits are quite reasonable considering the small size of the data bases for these complex product/time dependencies. The kinetic analysis for these systems is summarized in Table 2.

Analysis of kinetic data for converted coal; product oil and gas formed; and preasphaltene and asphaltene loss are shown in Figures 11 to 14. The oil

and gas data are seen to be described by equation 2 and 3 respectively. The converted coal data follows the expected behavior predicted by equation 11. The preasphaltene and asphaltene equations 5 and 6 respectively, will reduce to forms analogous to equations 3, 7 and 11 when the formation of these products is negligible. Despite the experimental scatter in some of the original data for these products, the fits of the equations to the data are in general quite reasonable. Thus, to within experimental error, the CDC mechanism describes the various reactant/product time behaviors. Table 3 lists the kinetic analysis results for these systems. Figures 9d and 9e show the Arrhenius plots for Shalabi's and Cronauer's rate constants respectively.

From the results in Tables 2 and 3, the rate constant ranges for preasphaltene, asphaltene, oil and gas formations are 1.0 to 56.0 min^{-1} , 0.01 to 0.1 min^{-1} , 0.002 to 0.1 min^{-1} and 0.007 to 0.2 min^{-1} respectively over the 350° to 450°C range. The rate constant ranges for preasphaltene and asphaltene disappearance are 0.03 to 0.09 min^{-1} and 0.005 to 0.06 min^{-1} respectively. Based on the quality of the mechanistic fit to the reported coal liquefaction kinetic data, which as shown in Table 5 cover a diverse range of reaction conditions, coal types and donor solvent compositions, it is proposed that the donor solvent/thermal bond cleavage/hydrogen capping mechanism provides a good, quantitative description of the rate limiting process. Furthermore the mechanism unifies the diverse coal kinetic data by using a set of common reaction sequences and thereby creates a common base for intercomparison, interpretation and evaluation of conversion for the broad range of processes currently being investigated in the coal liquefaction field.

The Liquefaction Transition State

Table 4 lists the Arrhenius parameters derived from the least squares analyses of the plots in Figure 9. According to transition state theory, the temperature (T) dependence of a rate constant (k) obeying the Arrhenius equation

$$k = A_a e^{-E_a/RT} \quad (12)$$

where E_a is the activation energy and R is the gas constant, can be interpreted in terms of the thermodynamics of activated complex formation:

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (13)$$

$$\Delta G^\ddagger = -RT \ln K^\ddagger \quad (14)$$

where $\Delta G^\ddagger$, $\Delta H^\ddagger$, $\Delta S^\ddagger$ and $K^\ddagger$ are respectively the free energy, enthalpy, entropy and equilibrium constant for activated complex formation. For a unimolecular reaction in solution

$$\Delta H^\ddagger = E_a - RT \quad (15)$$

and the transition state equation

$$k = \frac{k' T}{h} e^{\Delta G^\ddagger}$$

becomes

$$k = \frac{k'T}{h} e^{(\Delta S^\ddagger + R)/R} e^{-E_a/RT} \quad (16)$$

where k' is Boltzmann's constant and h is Planck's constant. In the present system the standard state for the unimolecular reaction given by reaction 1 is defined as 400°C. The $\Delta H^\ddagger$ values in table 4 were calculated using equation 15. Equating the terms of equation 12 and 16 yields the $\Delta S^\ddagger$ values in table 4. The $\Delta G^\ddagger$ values calculated using equation 13 netted an average value of 52 kcal which, according to equation 14, yields a $K^\ddagger$ value 1.3×10^{-17} .

The CDC mechanism proposes the disappearance of the $R-R/(H)_n$ complex is a unimolecular reaction as depicted by reaction 1 and described by equation 1. According to transition state theory, the rate limiting step in the conversion of a complex to products can be visualized as

where $C^\ddagger$ is the transition state. The slow step in the $C^\ddagger$ transition state formation involves both changes in the physical bonds of the solvent cage $(H)_n$ and chemical $R-R'$ bond cleavage processes. The systems showing low $\Delta H^\ddagger$ values (10-12 kcal or lower) are a result of having a physically controlled, as opposed to chemically controlled, rate limiting process in the activated complex formation. The physical rearranging of the donor $(H)_n$ and the bond to be cleaved $R-R$ into the $C^\ddagger$ configuration required for lowering the bond energy sufficiently to achieve cleavage and prevent recombination is the slow process for these systems. The high $\Delta H^\ddagger$ systems are interpreted as indicating the rate limiting

process is chemically controlled. That is, the cleavage of the $C^\ddagger$ transition state bond is the slow process. The observed change in entropy is consistent with the above arguments since the largest $\Delta S^\ddagger$ values are for the physically controlled systems. The average $\Delta S^\ddagger$ value for the physically controlled transition state reactions is $-63 \text{ cal/}^\circ\text{K}$ with a standard deviation of $4 \text{ cal/}^\circ\text{K}$. The consistent free energy value obtained for the eight different systems in Table 4 is taken as evidence that the overall reactant complex $R-R/(H)_n$ to activated complex $C^\ddagger$ transition is similar for these diverse liquefaction systems.

Further insight into the mechanism is gained if one considers the radical recombination reaction

which is the reverse of reaction 1. This reaction should play a significant role in systems where the hydrogen donor species are not in excess. In poor donor solvent systems, the differential rate law becomes

$$\frac{-d(R-R'/(H)_n)}{dt} = \frac{k_2}{k_{-1} + k_2} k_1 (R-R'/(H)_n)$$

This rate law reduces to the rate law

$$\frac{-d(R-R'/(H)_n)}{dt} = k_i (R-R'/(H)_n)$$

whenever $k_2 \gg k_{-1}$. There are two definable processes which give rise to the

$k_2 \gg k_{-1}$ condition. One involves the formation of reactive radical(s) in reaction 1 which extract hydrogen at a rate much faster than the above recombination reaction. This would correspond to a chemically controlled system. The other case occurs when there is a large energy barrier created which prevents radical recombination and thereby effectively prevents the recombination reaction. The physical rearrangement of the solvent cage during the bond cleavage process can be interpreted as giving rise to an energy barrier which impedes recombination. The thermodynamic results in Table 4 thus give insight into the relative role of these two processes for a given liquefaction system.

Insight into the hydrogen capping reaction following the thermal cleavage step of reaction 1 is gained from recent radical scavenger work.³² The addition of the radical scavenger benzoquinone to coal/tetralin systems results in conversion yield decreases of, on the average, 30% over the 400 to 470°C range. Thus, the radical scavenger can compete with the tetralin hydrogens for the $R^\bullet$ species. This observable competition suggests that the cleavage and capping steps are distinct from one another. This result coupled with the previously discussed evidence supporting complexing by the donor solvent suggests the complex does not involve the donatable solvent hydrogens directly. One could speculate that cleavage of the bond involves complexing with the aromatic portion of the hydroaromatic donor followed by a rearrangement step. The reported poor donor solvent properties of decalin,^{10,42} which does not have the tetralin aromatic ring, is consistent with this argument.

Figure 1. (a) - coal cluster model and general product formation reactions for coal conversion where R is any organic structure composed of any arrangement of the four product classes: preasphaltene(P), asphaltene(A), oil(L) or gas(G) consistent with class solubility. The subscripts denote d - conversion of, f - formation of, p - preasphaltene parameter, a - asphaltene parameter, l - oil parameter and g - gas parameter. The $\Delta/(H)_n$ denotes thermal cleavage and hydrogen capping of a complexed bond site (see mechanism section); (b) - common curvature of benzene soluble plus gas product yields vs. time plots, data taken from references 6 (diamond), 28 (square) and 49 (triangle); (c) - kinetic data and mechanistic fit for the tetralin system; (d) - characteristic time plots for the gas or oil yields based on equations 3 or 7 respectively, the numbers next to each curve are respectively the G' and k values used to calculate the curve; (e) - characteristic time plots for the preasphaltene yields based on equation 5, the numbers next to each curve are respectively the k' and k'' values used to calculate the curve; (f) - characteristic time plots for the asphaltene yields based on equation 6, the numbers next to each curve are respectively the k' and k'' values used to calculate the curve.

Figure 2. Fit of equation 11 to Hill's benzene soluble plus gas data taken from reference 6. The straight lines are the result of linear regression analysis of the data which yielded the cited slopes and deviations in slope.

Figure 3. Linear regression analysis of Hill's (ref. 6), Wiser's (ref. 3), Guin's (ref. 23) and Maekawa's (ref. 28) benzene solubility data based on equation 11.

Figure 4. Linear regression analysis of Guin's (ref. 44), Fisher's (ref. 58), Maekawa's (ref. 28) and Curran's (ref. 10) benzene solubility data based on equation 11.

Figure 5. Linear regression analysis of Neavel's (ref. 49) and Fant's (ref. 21) benzene solubility data based on equation 11.

Figure 6. Linear regression analysis of Storch's (ref. 18,19) and Gun's (ref. 31) benzene solubility data based on equation 11.

Figure 7. Linear regression analysis of Gun's (ref. 31) and Liebenberg's (ref. 13) benzene solubility data based on equation 11.

Figure 8. Linear regression analysis of Liebenberg's (ref. 13) benzene solubility data based on equation 11.

Figure 9. Arrhenius plots of rate constant data and linear regression analysis fit. See Table 4 for literature citation, symbol code key and calculated fit.

Figure 10. Nonlinear regression analysis and resultant numerical forms of equations 5, 6 and 10 for various conversion studies reported in the literature. See Table 2 for literature citations and related information.

Figure 11. Linear regression analysis of specific product classes based on equations 3, 5, 6, 7 and 11. See Table 3 and text for specifics.

Figure 12. See Figure 11 caption.

" 13. " " " "

" 14. " " " "

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Table 1. The linear regression analyses, rate constants, data ranges and related information for the benzene soluble kinetic data shown in Figures 2 to 8.

Reference	Figure	(T°C)	A _{fo} [#] (%)	k _{fa} x 10 ³ [#] (min ⁻¹)	k _{fa} Std. Dev. (10 ³ min ⁻¹)	Coal Conversion (%)		
						Initial	Final	Range
Hill-6	2-a	350	73	3.11	0.14	22	73	70
Hill-6	2-b	375	85	4.31	0.18	40	85	53
Hill-6	2-c	400	90	9.57	0.52	30	90	67
Hill-6	2-d	-	92	9.9	1.6	69	92	25
Hill-6	2-e	410	91	13.3	0.9	43	91	53
Hill-6	2-f	420	92	13.0	0.3	68	92	26
Hill-6	2-g	430	93	11.3	0.2	68	93	27
Hill-6	2-h	440	93	16.5	0.1	80	93	14
Hill-6	3-a	450	96	13.2	0.1	88	96	8
Hill-6 (two stage) ^a	3-b	400	78	7.32	0.05	47	78	40
Hill-6 (two stage) ^a	3-c	420	80	10.3	0.2	46	80	43
Hill-6 (two stage) ^a	3-d	440	84	45.6	3.8	55	84	35
Wiser-3	3-e	410	100 ^b	14.4	1.3	49	96	47
Guin-23	3-f	385	95 [*]	21.5	3.5	66	92	27
Guin-23	3-g	410	96 [*]	31.2	8.8	71	95	25
Maekawa-28 (220 atm H ₂)	3-h	400	95 [*]	18.5	2.3	59	92	35
Guin-44 (untreated) ^c	4-a	410	90 [*]	31.3	2.1	62	89	27
Guin-44 (demin.) ^d	4-b	410	70 [*]	17.7	2.2	48	67	19
Guin-44 (slurried) ^e	4-c	410	80 [*]	32.1	6.1	53	79	26

Table 1 (cont'd)

Reference	Figure	(T °C)	A _{F0} [#] (%)	k _{FA} × 10 ³ [#] (min ⁻¹)	k _{FA} Std. Dev. (10 ³ min ⁻¹)	Coal Conversion (%)		
						Initial	Final	Range
Fisher-58	4-d	400	97*	6.00	0.77	72	96	24
Mackawa-28 (160 atm H ₂)	4-e	400	95*	10.6	0.04	72	83	12
Mackawa-28 (110 atm H ₂)	4-f	400	95*	8.5	1.3	46	78	34
Curran-10	4-g	354	95*	16.8	2.4	42	75	33
Curran-10	4-h	388	95*	39.4	8.5	40	91	51
Neavel-49 (Sub-B coal)	5-a	400	91*	33.5	7.6	20	64	48
Neavel-49 (Lig. coal)	5-b	400	91*	33.1	1.3	38	70	35
Neavel-49 (HVB coal)	5-c	400	91*	20.0	3.7	13	47	37
Neavel-49 (HVCB Coal)	5-d	400	91*	31.7	5.3	27	66	43
Neavel-49 (LVB Coal)	5-e	400	91*	7.1	1.0	4	12	9
Neavel-49 (HVB Coal)	5-f	400	91*	15.9	1.1	6	36	33
Fant-21 (Wyodak coal)	5-g	449	55*	3.80	0.72	36	52	16
Fant-21 (Buelah coal)	5-h	449	55*	5.23	0.69	29	48	19
Storch-18,19	6-a	400	95*	2.27	0.43	57	90	33
Storch-18,19	6-b	385	95*	1.18	0.27	42	73	41
Storch-18,19 (SnS catalyst)	6-c	400	95*	10.2	1.3	64	88	24
Storch-18,19 (SnS catalyst)	6-d	385	95*	6.19	0.79	52	89	37
Storch-18,19 (SnS catalyst)	6-e	370	95*	4.33	0.71	45	90	47

Table 1 (cont'd)

Reference	Figure	(T°C)	A _{fo} [#] (%)	k _{fa} × 10 ^{3#} (min ⁻¹)	k _{fa} Std. Dev. (10 ³ min ⁻¹)	Coal Conversion (%)		
						Initial	Final	Range
Gun-31 (system 2) ^f	6-f	410	100	17.9	1.1	68	98	30
Gun-31 (system 2) ^f	6-g	400	100	13.8	0.6	68	97	29
Gun-31 (system 2) ^f	6-h	390	100	14.2	0.4	68	95	27
Gun-31 (system 1) ^g	7-a	410	100	21.5	0.4	68	99	31
Gun-31 (system 1) ^g	7-b	400	100	22.2	0.6	68	99	31
Gun-31 (system 1) ^g	7-c	390	100	22.4	0.3	68	99	31
Gun-31 (system 1) ^g	7-d	380	100	15.1	0.8	68	94	26
Liebenberg-13 (160 bar H ₂)	7-e	380	100	4.33	0.17	6	63	57
Liebenberg-13 (160 bar H ₂)	7-f	400	100	4.41	0.33	6	70	64
Liebenberg-13 (160 bar H ₂)	7-g	420	100	4.79	0.34	10	58	48
Liebenberg-13 (160 bar H ₂)	7-h	440	100	11.3	0.7	9	86	77
Liebenberg-13 (180 bar H ₂)	8-a	380	100	2.84	0.34	16	46	30
Liebenberg-13 (180 bar H ₂)	8-b	400	100	3.25	0.21	8	51	43
Liebenberg-13 (180 bar H ₂)	8-c	420	100	4.77	0.64	11	67	56
Liebenberg-13 (180 bar H ₂)	8-d	440	100	15.3	0.9	4	90	86
Liebenberg-13 (200 bar H ₂)	8-e	380	100	4.77	0.14	11	58	47

Table 1 (cont'd)

Reference	Figure	(T°C)	A _{fo} [#] (%)	k _{fa} x 10 ^{3#} (min ⁻¹)	k _{fu} Std. Dev. (10 ³ min ⁻¹)	Coal Conversion (%)		
						Initial	Final	Range
Liebenberg-13 (200 bar H ₂)	8-f	400	100	3.64	0.49	12	64	52
Liebenberg-13 (200 bar H ₂)	8-g	420	100	10.8	1.2	31	85	54
Liebenberg-13 (200 bar H ₂)	8-h	440	100	8.69	0.68	10	76	66

- treatment based on equation 9

* - approximated values

a - reaction run on coal residue left after annealing coal in tetralin at 250°C and extracting with benzene

b - original paper reported data in normalized form

c - nominally processed coal, sieved and dried before running reaction

d - coal demineralized using high intensity magnetic separator before running reaction

e - coal slurried with water and dried before running reaction

f - coal reacted in presence of tetralin and hydrogen

g - coal reacted in presence of tetralin, ammonium molybdate catalyst and hydrogen.

Table 2. The nonlinear regression analysis, rate constants, data ranges and related information for the kinetic data shown in Figure 10.

Reference	Figure	(T°C)	X _{fo} (%)	k _f × 10 ³ (min ⁻¹)	k _f Std. Dev. (10 ³ min ⁻¹)	X' _{fo} (%)	k' _f × 10 ³ (min ⁻¹)	k' _f Std. Dev. (10 ³ min ⁻¹)	Coal Conversion (%)		
									Initial	Final	Range
Neavel-49 (HVCB coal) ^{a, #}	10-a	400	65.7	164.	1.	34.3	13.0	0.3	5	91	86
Neavel-49 (HVCB coal) ^{b, #}	10-b	400	98.7	1080.	5.	1.4	11.	16.	40	98	58
Whitehurst-41 (wyodak coal) ^{b, #}	10-c	427	37.3	56300.	490.	62.3	51.8	0.3	12	75	63
Storch ^{a, #} -18, 19	10-d	400	73.*	22.1	0.1	19.*	2.38	0.02	57	90	33
Storch-18, 19 (SnS catalyst) ^{a, #}	10-e	385	73.*	16.7	0.1	19.*	3.76	0.03	52	92	40
Storch-18, 19 (SnS catalyst) ^{a, #}	10-f	400	73.	28.9	0.6	19.	7.19	0.43	64	93	29
Cronauer-7 (HPH solvent) ^c	10-g	400	100.*	75.0	0.4	100.*	46.4	0.3	51	79	28
Fu-59 (H ₂ gas) ^c	10-h	400	95.*	41.1	0.1	95.*	8.26	0.02	35	94	59
Fu-59 (synthesis gas) ^c	10-i	400	95.*	36.4	0.1	95.*	9.06	0.02	34	85	51
Shalabi ^d -17	10-j	375	90.*	48.8	1.2	90.*	12.3	0.1	50	82	32

* - assumed value

- treatment based on equation 10: $X_{fo} = B_{fo}$, $k_f = k_{fb}$, $X'_{fo} = A_{fo}$, $k'_f = k_{fa}$

a - total benzene soluble plus gas data

b - total pyridine soluble plus gas data

c - yield of product soluble in benzene but insoluble in hexane, eg. asphaltenes, therefore treatment based on equation 6:
 $X_{fo} = A_{fo}$, $k_f = k_{fa}$, $X'_{fo} = A_{co}$, $k'_f = k_{ca}$

d - preasphaltene product yield therefore treatment based on equation 5: $X_{fo} = P_{fo}$, $k_f = k_{fp}$, $X'_{fo} = P_{co}$, $k'_f = k_{cp}$; kinetic data uniformly time shifted by +5 minutes to avoid t=0 anomaly of exponential, note the assignment of t=0 to the initial data is arbitrary due to the warm up time.

Table 3. The linear regression analyses, rate constants, data ranges and related information for the kinetic data shown in Figures 11 to 13.

Reference	Figure	T(°C)	X_{f0}^* (%)	$k_f \times 10^3$ (min ⁻¹)	k_f Std. Dev. (10 ³ min ⁻¹)	Product
Cronauer-7 (HPII solvent)	11-a	450	100	80.	34.	coal converted ^a (80,99,19) ^f
Cronauer-7 (HPII solvent)	11-b	450	100	88.8	7.1	preasphaltene ^b
Cronauer-7 (HPII solvent)	11-c	450	100	64.	15.	asphaltene ^c
Cronauer-7 (HPII solvent)	11-d	450	74	116.	36.	oil ^d
Cronauer-7 (HPII solvent)	11-e	450	26	165.	23.	gas ^e
Cronauer-7 (HPII solvent)	11-f	400	100	20.4	3.4	coal converted ^a (51,79,28) ^f
Cronauer-7 (HPII solvent)	11-g	400	100	34.	10.	preasphaltene ^b
Cronauer-7 (HPII solvent)	11-h	400	74	26.0	2.5	oil ^c
Cronauer-7 (HPII solvent)	12-a	400	26	8.9	3.5	gas ^e
Cronauer-7 (HIAO solvent)	12-b	450	95	31.	14.	coal converted ^a (67,89,22) ^f
Cronauer-7 (HIAO solvent)	12-c	450	34	28.	11.	gas ^e
Cronauer-7 (HIAO solvent)	12-d	400	90	22.6	7.9	coal converted ^a (50,74,24) ^f
Cronauer-7 (HIAO solvent)	12-e	400	90	33.	11.	preasphaltenes ^b
Cronauer-7 (HIAO solvent)	12-f	400	90	4.7	5.7	asphaltenes ^c
Cronauer-7 (HIAO solvent)	12-g	400	55	21.3	1.6	oil ^d
Cronauer-7 (HIAO solvent)	12-h	400	35	7.0	8.7	gas ^e

Table 3 (cont'd)

Reference	Figure	T(°C)	X_{fo}^* (%)	$k_f \times 10^3$ (min ⁻¹)	k_f Std. Dev. (10 ³ min ⁻¹)	Product
Shalabi-17	13-a	400	90	10.8	3.2	coal converted ^a (66,87,21) ^f
Shalabi-17	13-b	400	90	4.13	0.7	preasphaltenes ^b
Shalabi-17	13-c	400	90	6.5	3.5	asphaltenes ^c
Shalabi-17	13-d	400	60	5.35	0.66	oil ^d
Shalabi-17	13-e	375	90	8.4	3.1	coal converted ^a (50,82,32) ^f
Shalabi-17	13-f	375	90	1.52	0.45	asphaltenes ^c
Shalabi-17	13-g	375	60	2.28	0.77	oil ^d
Shalabi-17	13-h	350	90	7.48	0.22	coal converted ^a (40,74,34) ^f
Shalabi-17	14-a	350	90	0.78	0.42	preasphaltene ^b
Shalabi-17	14-b	350	90	0.54	0.05	asphaltene ^c
Shalabi-17	14-c	350	60	2.51	0.51	oil ^d
Fu-59 (H ₂ gas)	14-d	400	95	33.4	2.6	coal converted ^a (35,94,59) ^f
Fu-59 (H ₂ gas)	14-e	400	35	12.5	3.0	oil ^d
Fu-59 (synthesis gas)	14-f	400	95	13.9	2.9	coal converted ^a (34,85,51) ^f _a
Fu-59 (synthesis gas)	14-g	400	35	7.7	2.8	oil ^d

* - approximated values

a - treatment based on equation 11 where: $X_{fo} = A_{fo}$, $k_f = k_{fa}$

b - treatment based on the reduced form of equation 5: $P = -P_{co} (1 - e^{-k_{cp}t})$; $X_{fo} = P_{co}$, $k_f = k_{cp}$

c - treatment based on the reduced form of equation 6: $A = -A_{co} (1 - e^{-k_{ca}t})$; $X_{fo} = A_{co}$, $k_f = k_{ca}$

d - treatment based on equation 7: $X_{fo} = L_{fo}$, $k_f = k_{fl}$

e - treatment based on equation 3: $X_{fo} = G_{fo}$, $k_f = k_{fg}$

f - the numbers in parenthesis are the percent values for the initial, final and range over which the coal conversion was studied at a given temperature

Table 4. Symbol code, Arrhenius parameters/standard deviations and transition state thermodynamic values derived from the least squares analyses of the plots in Figure 9. Standard state: 400°C.

Reference	Figure	Symbol	Ranges		$\ln A_a$	E_a (kcal)	$\Delta H^\ddagger$ (kcal)	$\Delta S^\ddagger$ (cal./°K)	$\Delta G^\ddagger$ (kcal)
			T(°C)	Conver. %					
Hill-6	9-a	⊞	350-410	53-70	10.9 $\pm$ 2.5	20.8 $\pm$ 3.3	20	-49	53
Hill-6 (two stage)	9-a	+	400-440	35-40	22.0 $\pm$ 6.7	36.2 $\pm$ 9.3	35	-27	53
Guin-23*	9-a	⊙	385-410	25-27	6.3	13	12	-58	51
Curran-10*	9-a	⊕	354-388	33-51	13	21	20	-45	50
Storch-18,19* (partial range)	9-b	⊞	385-400	33-41	23	38	37	-26	55
Storch-18,19 (partial range, SnS Cat.)	9-b	+	370-400	24-47	13.8 $\pm$ 2.0	24.7 $\pm$ 2.6	23	-43	52
Storch-18,19* (full range, k ₁ , SnS Cat.)	9-b	⊕	385-400	29-40	20	32	31	-30	51
Storch-18,19* (full range, k ₂ , SnS Cat.)	9-b	⊙	385-400	29-40	23	38	37	-24	53
Gun-31 (system 1)	9-c	⊕	380-410	26-31	3 $\pm$ 5	9.5 $\pm$ 6.4	8	-60	50
Gun-31 (system 2)	9-c	⊞	390-410	27-30	4 $\pm$ 6	10 $\pm$ 10	9	-60	50
Liebenberg-13 (160 bar)	9-c	△	380-440	48-77	5 $\pm$ 5	13.5 $\pm$ 6.9	12	-60	50
Liebenberg-13 (180 bar)	9-c	▽	380-420	30-56	3.1 $\pm$ 2.5	11.7 $\pm$ 3.4	10	-64	53
Liebenberg-13 (200 bar)	9-c	±	380-440	47-66	5 $\pm$ 6	13.4 $\pm$ 8.7	12	-60	50
Shalabi-17 (conver.)	9-d	⊞	350-400	21-34	0.4 $\pm$ 0.9	5.6 $\pm$ 1.2	4.3	-70	50
Shalabi-17* (preasph.)	9-d	△	350-400	21-34	15	28	27	-40	54
Shalabi-17 (asph.)	9-d	±	350-400	21-34	25.9 $\pm$ 3.9	41.4 $\pm$ 5.0	40	-19	53

Table 4 (cont'd)

Reference	Figure	Symbol	Ranges		$\ln A_a$	E_a (kcal)	$\Delta H^\ddagger$ (kcal)	$\Delta S^\ddagger$ (cal./°K)	$\Delta G^\ddagger$ (kcal)
			T(°C)	Conver. %					
Shalabi-17 (oil)	9-d	⊕	350-400	21-34	4+7	12.4+9.5	11	-63	53
Cronauer-17* (HPH/conver.)	9-e	⊞	400-450	19-28	16	26	25	-39	51
Cronauer-17* (HPH/preasph.)	9-e	⊠	400-450	19-28	10	19	18	-49	51
Cronauer-7* (HPH/oil)	9-e	⊕	400-450	19-28	18	29	28	-35	52
Cronauer-7* (HPH/gas)	9-e	▽	400-450	19-28	37	56	55	+4.2	52
Cronauer-7* (HAO/conver.)	9-e	⊞	400-450	22-24	0.8	6.1	4.8	-69	51
Cronauer-7* (HAO/gas)	9-e	▽	400-450	22-24	15	27	26	-40	53
Average									52
Std. Dev.									1

*The error for these calculated parameters is unknown because the data sets consist of only two datum. Two significant figures were arbitrarily assumed to be significant.

Table 5. Description of coal systems, donor solvents and liquefaction conditions for literature data analyzed for Tables 1 to 3.

Reference	Figure	Coal	Proximate Analysis (dry weight basis)			Donor Solvent	Hydrogen Pressure (PSI) at Temperature (°C)
			VM	FC	A		
Wiser-3, Hill-6	2-a to 3-e	high volatile bituminous, Utah Spring Canyon coal mine	45.7	45.9	8.4	tetralin	-
Cronauer-7	10-g, 11-a to 12h	subbituminous, Belle Ayr Mine, Wy.	40.5	49.4	10.1	hydrogenated anthracene (HAO); hydrogenated phenanthrene (HPH)	2000 psi @ 400, 450°C
Curran-10	4-g,h	Ireland Mine, West Virginia	42.8	45.8	11.4	tetralin	-
Liebenberg-13	7-e to 8-h	bituminous, South Africa	37.9	54.4	13.7	tetralin	2320-2900 psi @ 380 to 440°C
Shalabi-17	13a to 14-c, 10j	Madisonville No. 9 seam, Fies Mine, Kt.	31.8	43.0	25.2	tetralin	2000 psi @ 350 to 400°C
Storch-18,19	6-a to 6-e, 10-d to 10-f	Bruceton, Pa.; tin sulfide catalyst	38.8	54.9	6.3	tetralin	1000 psi @ 20°C
Fant-21	5-g,h	Wyodak Bueluk	-	-	-	hydrogenated recycle solvent	-
Guin-23,44	3-f,g 4-a to 4-c	Kentucky No. 9/14	-	-	-	creasote oil	1000-2600 psi @ 410°C
Maekawa-28	3h, 4-e,f	Brown coal from Hokkaido; red mud catalyst	51.0	41.7	7.3	anthracene oil	1620-3230 psi @ 400°C
Gun-31	6-f to 7-d	coal from Makun field, Assam; ammonium molybdate catalyst	44.3	52.7	3.0	tetralin	3100 psi @ 380-410°C
Whitehurst-41	10-c	Wyodak coal from Bell Ayr Mine, Wy.	47.4	47.9	3.6	Synthetic solvent (81% tetralins)	1000 to 1400 psi at 427°C

Table 5 (cont'd)

Reference	Figure	Coal System	Proximate Analysis (dry weight basis)			Donor Solvent	Hydrogen Pressure (PSI) at Temperature (°C)
			VM	FC	A		
Neavel-49	5-a	sub-bituminous	41.0	53.4	5.6	hydrogenated creasote oil	-
	5-b	lignite	46.0	44.5	9.5	hydrogenated creasote oil	-
	5-c	high volatile B bituminous	38.0	44.9	17.1	hydrogenated creasote oil	-
	5-d	high volatile C bituminous	45.0	43.0	12.0	hydrogenated creasote oil	-
	5-e	low volatile bituminous	16.0	73.0	11.0	hydrogenated creasote oil	-
	5-f	high volatile A bituminous	37.0	45.8	17.2	hydrogenated creasote oil	-
	10-a,b	high volatile C bituminous	45.0	50.7	4.3	tetralin	-
Fisher-58	4d	Washington Anthraxylon, King County	40.5	58.0	1.5	tetralin	1000 psi @ 20°C
Fu-59	10-h,i, 14-d to 14-g	Kentucky bituminous				Alkyl-naphthalene oil	3000 psi @ 400°C

1a

COAL CLUSTERS

R-P-P	R-A-A	R-L-L	R-G-G
R-P-A	R-A-L	R-L-L	
R-P-L	R-A-G	R-L-G	
R-P-G

400 C/NEAVEL/BENZENE SOL. + GAS/COAL: d HVCB

$$XX = 65.7(1-EXP(-0.164t)) + 34.3(1-EXP(-0.0130t))$$

400 C/NEAVEL/PYRIDINE SOL. + GAS/ COAL: d HVCB

$$XX = 98.6(1-EXP(-1.08t)) + 1.36(1-EXP(-0.0105t))$$

427 C/WHITEHURST/PYRIDINE SOL. / COAL: WYODAK

$$XX = 37.3(1-EXP(-56.3t)) + 62.3(1-EXP(-0.0518t))$$

400 C / BZ SOL. / STORCH

$$X = 73(1-EXP(-1.33t)) + 19(1-EXP(-0.143t))$$

385 C / BZ SOL. / STORCH / SsS CATALYST

$$X = 73(1-EXP(-1.002t)) + 19(1-EXP(-0.2256t))$$

400 C / BZ SOL. / STORCH / SsS CATALYST

$$X = 73(1-EXP(-1.73t)) + 19(1-EXP(-0.431t))$$

400 C / CRONAUER / ASPHALTENES / HPH

$$A = 100(1-EXP(-0.075X)) - 100(1-EXP(-0.0464X))$$

400 C / ASPHALTENES / FU / HYDROGEN GAS

$$A = 0.95(1-EXP(-0.0411t)) - 0.95(1-EXP(-0.00826t))$$

400 C / ASPHALTENES / FU / SYNTHESIS GAS

$$A = 0.95(1-EXP(-0.0364t)) - 0.95(1-EXP(-0.00906t))$$

375 C / PREASPHALTENES / SHALABI

$$P = 0.98(1-EXP(-0.048t)) - 0.98(1-EXP(-0.0123t))$$