

PERICYCLIC PATHWAYS IN THE MECHANISM OF COAL LIQUEFACTION

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1. INTRODUCTION

The object of this paper is to draw attention to the possible importance of concerted molecular reactions, of the type termed pericyclic by Woodward and Hoffman (1), in the mechanism of coal liquefaction.

In outline of what follows we will begin by brief reference to previous work on coal liquefaction. The present approach will then be motivated from considerations of coal structure and hydrogen-donor activity. A theoretical section follows in the form of a pericyclic hypothesis for the coal liquefaction mechanism, with focus on the hydrogen transfer step. Experiments suggested by the theory are then discussed, with presentation of preliminary results for hydrogen transfer among model substrates as well as for the liquefaction of an Illinois No. 6 coal to hexane-, benzene-, and pyridine-solubles by selected hydrogen donors.

Previous literature on coal liquefaction is voluminous (2). Molecular hydrogen at elevated pressures is effective (3) but more recent work has employed hydrogen donor 'solvents', such as tetralin (4), which are capable of liquefying coal at relatively milder conditions. Donor effectiveness is strongly dependent upon chemical structure. Thus, among hydrocarbons, several hydroaromatic compounds related to tetralin  are known to be effective (5,6,7,8), while the corresponding fully aromatic  or fully hydrogenated  compounds are relatively ineffective (7,9). Further, among alcohols, isopropanol HO- and o-cyclohexyl phenol HO- are effective donors (7) whereas t-butanol HO- is not (10). These observations have been theoretically attributed (e.g. 2,9) to a free-radical mechanism according to which, during liquefaction, certain weak bonds break within the coal substrate, forming radical fragments which abstract hydrogen atoms from the donor, thereby becoming stable compounds of lower molecular weight than the original coal. According to this free-radical mechanism, therefore, donor effectiveness is related to the availability of abstractable hydrogen atoms, and this notion seems to have won general acceptance in the literature because it rationalizes the effectiveness of tetralin, which possesses benzylic hydrogen atoms, relative to naphthalene and decalin, which do not. However, the foregoing mechanism is less than satisfactory because indane , which has just as many benzylic hydrogens as tetralin, is relatively ineffective (7) as a donor. Also, the activity of the alcohol donors, like isopropanol, would have to involve abstraction of hydrogen atoms bonded either to oxygen or to an sp³-hybridized carbon; this seems unlikely because both of these bonds are relatively strong compared to any that the hydrogen might form with a coal fragment radical.

The present approach to the coal liquefaction mechanism evolved from contemporary knowledge of coal structure (e.g. 11,12,13), which emphasizes the existence of hetero-atom-containing hydroaromatic structures comprising 2- to 4-ring fused aromatic nuclei joined by short methylene bridges. From this it is apparent that sigma bonds between sp³-hybridized atoms in coal are seldom more than one bond removed from either a pi-electron system or a hetero-atom containing substituent. Such a molecular topology is favorable for pericyclic reactions, which are most prone to occur on skeletons with proximal pi- and sigma-bonds activated by substituents. We therefore hypothesize that the overall interaction between the coal substrate and hydrogen donor, which eventually leads to liquefaction, involves a sequence of concerted, pericyclic steps. (Appropriate steps will be detailed in the next

section.) The novelty of this approach is twofold; first, the mechanistic concept is essentially different from any that has hitherto been proposed in coal-related literature and second, it lends itself to quantitative tests and predictions since the pericyclic reactions envisioned must obey the Woodward-Hoffman rules (1) for the conservation of orbital symmetry. It should also be pointed out that if the present approach proves valid, then it will have the engineering significance that the large volume of recently developed pericyclic reaction theory (14, 15,16) could be applied to the practical problem of defining and improving actual coal liquefaction processes.

2. THEORY

In delineating a coal liquefaction mechanism we distinguish three basic steps, namely rearrangements, hydrogen-transfer, and fragmentation, all of which are hypothesized to occur via thermally-allowed pericyclic reactions. Some typical reactions appropriate for each step are indicated below using Woodward-Hoffman (1) terminology:

Rearrangements: Sigmatropic shifts, electrocyclic reactions
 Hydrogen-Transfer: Group-transfers
 Fragmentation: Group-transfers, retro-ene, cyclo-reversions.

An illustration of how the overall pericyclic mechanism might apply to the decomposition of 1,2 diphenylethane, a model substrate, in the presence of Δ^1 -dihydronaphthalene, a model hydrogen-donor, has recently been given (17). In the present work, attention is focussed on the hydrogen-transfer step.

Hypothesis.

The transfer of hydrogen from donors to the coal substrate during liquefaction occurs by concerted pericyclic reactions of the type termed 'group transfers' by Woodward and Hoffman (1).

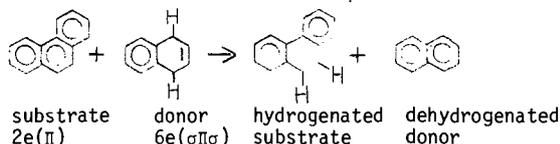
Consequences.

(A) Allowedness.

The Woodward-Hoffman rules (1) state that: A ground state pericyclic change is symmetry allowed when the total number of $(4q + 2)$ suprafacial and $(4r)$ antarafacial components is odd".

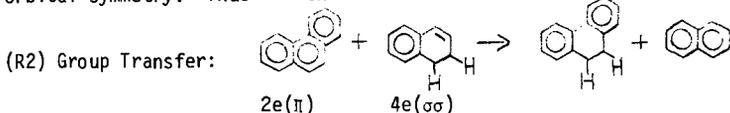
To illustrate how this applies in the present circumstances we consider a possible group transfer reaction between Δ^2 dihydronaphthalene, , a hydrogen donor, and phenanthrene, , a substrate (hydrogen acceptor) which models a polynuclear aromatic moiety commonly found in coal. In the overall group transfer reaction:

(R1) Group Transfer:

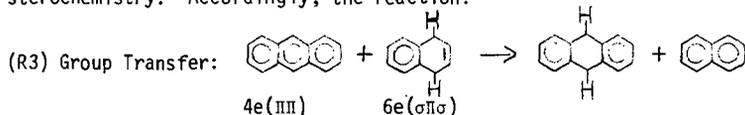


hydrogen is transferred from Δ^2 -dialin to the phenanthrene, producing 9,10 dihydrophenanthrene and naphthalene; this reaction is slightly exothermic, with $\Delta H_p^\circ \sim -8$ kcal as written. The electronic components involved are $2e(\pi)$ on the substrate and $6e(\sigma\pi\sigma)$ on the donor and from the Woodward-Hoffman rules it can be seen that the reaction will be thermally forbidden in either the supra-supra stereochemistry (which is sterically most favorable) or the antara-antara stereochemistry (sterically the most unfavorable) but will be thermally allowed in either the antara-supra or supra-antara modes, both of the latter being possible, but sterically difficult, stereochemistries. A reaction profile for (R1) is sketched in Figure 1, showing energy versus reaction coordinate as well as transition state stereochemistry for both the forbidden supra-supra and the allowed antara-supra modes. We note

next that changing the donor from Δ^2 -dialin  to Δ^1 -dialin , changes the donor electronically from a $6e(\sigma\pi\sigma)$ component to a $4e(\sigma\sigma)$ component, of contrary orbital symmetry. Thus for the overall reaction:



the supra-supra (and antara-antara) modes will be thermally allowed while the antara-supra (and supra-antara) modes are forbidden. The practical upshot of this is that the chemically very similar dialin isomers should exhibit strikingly different reactivities in concerted group transfers with a given substrate, on account of their opposite orbital symmetries. Note that no reasonable free-radical mechanism could predict profound differences in the donor capabilities of these dialin isomers. Orbital symmetry arguments can also be extended to differences in the substrates. Thus anthracene  is a $4e(\pi\pi)$ component, of symmetry opposite to that of phenanthrene , which is a $2e(\pi)$ component; therefore, with a given donor, such as Δ^2 -dialin , group transfers that are symmetry-forbidden with phenanthrene will be symmetry-allowed with anthracene in the same stereochemistry. Accordingly, the reaction:



is a $4e(\pi\pi) + 6e(\sigma\pi\sigma)$ group transfer, which is thermally-allowed in the supra-supra stereochemistry whereas the analogous reaction (R1) with phenanthrene was forbidden.

Generalization of the preceding suggests that there exist two basic classes of donors (and acceptors), of opposite orbital symmetries, which will respectively engage in group transfer reactions either as $(4n+2)$ electron components or as $(4n)$ electron components. Donors with $(4n+2)e$ will, in general, transfer hydrogen to $(4m+2)e$ acceptors, the most favorable supra-supra stereochemistry being presumed in each case. Among the $(4n+2)e$ class of hydrogen donors, the first ($n=0$) member is molecular hydrogen and the second ($n=1$) member is the but-2-ene moiety, while among the $(4n)e$ class of donors, the first ($n=1$) member is the ethane moiety, the second ($n=2$) the hexa-2,4-diene moiety. Among hydrogen acceptors, the $(4m+2)e$ class has the ethylene and hexa-1,3,5-triene moieties as its first two members, while the $(4m)e$ class of acceptors possesses the buta-1,3-diene and octa-1,3,5,7-tetraene moieties as its first two members. Each of the foregoing series can be continued straightforwardly for $n>2$.

Interestingly, the nature of allowed donor-acceptor interactions suggests that donor class will be conserved in any hydrogen transfer sequence. Thus a $(4n+2)e$ donor, say, will transfer hydrogen to a $(4m)e$ acceptor, and the latter, upon accepting the hydrogen, will evidently become a $(4m+2)e$ donor, of the same class as the original donor.

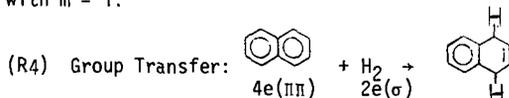
The donor and acceptor classes illustrated with hydrocarbons can be directly extended to include hetero-atoms. For example, the alcohol moiety  would be a $4e$ donor, of the same orbital symmetry as the ethane moiety . Similarly the carbonyl moiety $O=C$ would be a $2e$ acceptor, analogous to an ethylene moiety $=$ in terms of orbital symmetry. Thus hydrogen transfer reactions of molecules with hetero-atoms should have the same allowedness as reactions of their iso-electronic hydrocarbon analogues.

(B) Reactivity

The actual rates of thermally-allowed pericyclic reactions vary vastly, and

frontier-orbital theory (14,15,16) has proven to be the primary basis for quantitative understanding and correlation of the factors responsible. It is therefore of interest to find the dominant frontier orbital interactions for the group transfer reactions hypothesized to occur.

The HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied MO) levels for hydrogen donors used in coal liquefaction are not yet well known, but the principles involved can be illustrated with the group transfer reaction between molecular hydrogen, a $(4n+2)e$ donor with $n = 0$, and naphthalene, a $(4m)e$ acceptor with $m = 1$:



An approximate frontier orbital (FO) interaction diagram for this system is presented in Figure 2. This shows that the dominant FO interaction, i.e., that with the lowest energy gap, is between HOMO(H_2)-LUMO (); details of the interaction are given towards the bottom of the figure showing the respective phases and coefficients involved.

The preceding indications regarding the dominant FO interaction in hydrogen-transfer reactions suggests that they would be facilitated by a reduction in the HOMO (hydrogen donor)-LUMO (hydrogen acceptor) energy separation. Thus donor effectiveness should be enhanced by increasing the donor HOMO energy, e.g., by electron-releasing or conjugative substitution, whereas acceptor effectiveness should be enhanced by lowering the acceptor LUMO level, e.g. by electron-withdrawing or conjugative substitution, or by complexation with Lewis acids. As a practical example relevant to our experiments, we should expect Δ^2 -dialin to be a more effective $(4n+2)e$ type of hydrogen donor than tetralin because vinylic substitution in the former should raise the level of the hydrogen-containing HOMO. For the same reason, Δ^1 -dialin should also be a more effective $(4n)e$ type of donor than tetralin . Note that the Δ^1 - and Δ^2 -dialins have the opposite orbital symmetries; their reactivities cannot therefore be meaningfully compared, inasmuch as their reactions with a common acceptor cannot both be allowed.

3. EXPERIMENTS

(A) Model Compounds

From the theoretical discussion it follows that the present hypothesis for the hydrogen transfer mechanism can be tested by a study of reactions between hydrogen donors and acceptors of opposite orbital symmetries. Our experimental grid is shown in Table 1.1. The coal substrate was modelled by anthracene, a $(4m)e$ acceptor, and by phenanthrene, a $(4m+2)e$ acceptor; both of these aromatic C14 moieties exist in coal and are found in coal-derived liquids. The hydrogen donor solvent was modelled by a number of cyclic C10 compounds derived from naphthalene by hydrogenation. Among these, the Δ^1 - and Δ^2 -dialin isomers were of principal interest, being respectively hydrogen-donors of the $(4n+2)e$ and $(4n)e$ classes; the tetralin and decalin served as control solvents, the former being very commonly used in coal liquefaction experiments. For the 2×2 matrix of possible hydrogen-transfer reactions between the model C14 substrates and C10 dialin solvents, the Woodward-Hoffman rules predict that reaction in the favorable supra-supra stereochemistry should be thermally-allowed for (Δ^1 -dialin + phenanthrene) and (Δ^2 -dialin + anthracene) and thermally-forbidden for (Δ^1 -dialin + anthracene) and (Δ^2 -dialin + phenanthrene). These predictions are shown in Table 1.1 with \checkmark denoting the allowed and x the forbidden reactions.

The experiments were conducted batchwise in small stainless-steel pipe-bombs immersed in a molten-salt bath that was maintained at a desired, constant temperature. Pipe-bomb heat-up and quench times, on the order of 1 min each, were

negligible compared with reaction times, which were on the order of 1 hr. The reagents used were obtained commercially; all were of purity $\geq 98\%$ except for the Δ^2 -dialin which had a composition of (anthracene, phenanthrene, tetralin, decalin) = (7, 9, 20, 64) mol%. The proportions of substrate to solvent were maintained constant, with the C14 substrates as limiting reactants in all cases. The extent of reaction was measured by proton-NMR spectroscopy on samples of the whole reaction batch, as well as of each of the C10 and C14 fractions separated by vacuum distillation and liquid chromatography.

Experimental results are shown in Table 1.2, which quotes the observed percentage conversion of each of the model C14 substrates to their di-hydro derivatives by each of the model C10 solvents. Consider first the column for the anthracene substrate, showing its conversion to 9,10 dihydroanthracene after 2 hr at 300 C in various solvents. The conversion by tetralin (58%), is an order of magnitude greater than that by phenanthrene (5%), in striking accord with the theoretical predictions according to which the reaction with phenanthrene was allowed while that with tetralin was forbidden. Note too that conversions with the control solvents decalin (3%) and anthracene (no reaction) were less than those with the test solvents, verifying that the latter were indeed the more active. Reactions with phenanthrene substrate required rather more severe conditions, namely 2 hr at 400 C, than anthracene. While the lower reactivity of phenanthrene relative to anthracene is generally well known, in the present context it can directly be attributed to the phenanthrene possessing the higher energy LUMO. The conversions observed, phenanthrene (16%) > tetralin (10%), are in accord with theoretical predictions, and appreciably exceed the conversions obtained with the control solvents decalin (2%) and anthracene (no reaction). It is interesting that the observed selectivity of hydrogen-transfer from the Δ^1 - and Δ^2 -dialins to phenanthrene, respectively (0.6/1), is not as great as that to anthracene, respectively (12/1). Possible reasons for this are first that whereas anthracene is essentially always constrained to interact with supra-stereochemistry at its 9,10 positions, the phenanthrene structure admits a possible antarafacial interaction across its 9,10 positions and this latter might have permitted a thermally-allowed (antara-supra) hydrogen-transfer from Δ^2 -dialin. Second, the Δ^2 -dialin used contained some Δ^1 -dialin impurity, which could not contribute to anthracene conversion (forbidden) whereas it might have contributed to the phenanthrene conversion (allowed); third, the dialins have a tendency to disproportionate, to naphthalene and tetralin, at elevated temperatures and this might have influenced the results for phenanthrene, which were at the higher temperature.

In summary, the Δ^1 - and Δ^2 -dialin isomers have been shown to be appreciably more active than tetralin (and decalin) in transferring hydrogen to anthracene and phenanthrene. The observed selectivity of this hydrogen transfer is in accord with the Woodward-Hoffman rules for group transfer reactions, anthracene conversions being in the ratio (tetralin / phenanthrene) = 12/1 \gg 1 while phenanthrene conversions are in the ratio (tetralin / phenanthrene) = 0.6/1 < 1. The quantitative differences in the selectivities observed with anthracene and phenanthrene are being further explored.

(B) Coal Conversion

The dialin donor solvents were also used directly in coal liquefaction studies. Inasmuch as details of coal structure are unknown, the present theory can only be tested in a qualitative way, as follows. First, if the liquefaction of coal occurs under kinetic control with hydrogen-transfer from the donor solvent involved in the rate-determining step, then we should expect the dialin donors to be more effective than the control solvent tetralin (and also decalin). This is suggested by the theory because the dialins possess higher energy HOMOs than tetralin and according to the frontier-orbital analysis given previously, the hydrogen-transfer reactions of the dialins should therefore be kinetically favored relative to those of tetralin. Second, according to the present theory, donor symmetry is preserved during hydrogen transfer, i.e., a donor of a given class is capable only of interaction with acceptors of the complementary class. Now since the coal substrate likely contains hydrogen acceptors of both (4m)e and (4m+2)e classes, a

mixture of solvents containing donors of both (4n+2)e and (4n)e classes should be more effective in hydrogen transfer than a single solvent of either class which could interact with only one of the two possible classes in coal. Thus, in principle, for each coal there should exist an 'optimal' solvent which contains hydrogen donors of opposite symmetries in proportions that are matched to the proportions of the complementary hydrogen acceptors in the coal. For these reasons our theory suggests that a mixture of Δ^1 - and Δ^2 -dialins should be a better donor solvent than either the Δ^1 - or the Δ^2 -dialin alone, with the further indication that there may exist an optimal mixture composition that is characteristic of a given coal.

Liquefaction experiments were performed on a sample (18) of Illinois No. 6 coal, from Sesser, Illinois. Proximate and elemental analyses of this high volatile A bituminous coal are given in Table 2. The coal, of particle size 600-1200 microns (32x16 mesh), was dried at 110 C in a nitrogen blanketed oven prior to liquefaction. A solvent to coal weight ratio of 2.0 was used in all experiments, which were conducted in tubing bomb reactors that were immersed in a constant-temperature bath for the desired time while being rocked to agitate the reactor contents. At the end of each experiment, the reactors were quenched and their contents analyzed to ascertain the amounts of each of hexane-, benzene-, and pyridine-solubles (plus gas) produced from the original coal. The procedure used for all analyses is described for the pyridine-solubles (plus gas). First the reactor contents were extracted with pyridine and the residue dried on a pre-weighed ashless filter paper to provide the gravimetric conversion to pyridine-solubles, defined as $100(1-(\text{daf residue}/\text{daf coal}))$. Second, the residue was ashed in a furnace for 3 hours at 800 C, yielding the ash-balance conversion to pyridine solubles, defined as $100(1-(a/A))/(1-(a/100))$ where A and a were respectively the weight percentages of ash in the residue and in the original coal. The conversions obtained from each of the two methods normally agreed to within ± 2 weight percent and were averaged to provide final values.

Results showing the effectiveness of the Δ^1 - and Δ^2 -dialins in coal liquefaction relative to control solvents, naphthalene, decalin, and tetralin, are presented in Tables 3.1 and 3.2. In both these tables, each row provides the conversion of the coal sample to each of hexane-, benzene-, and pyridine-solubles (plus gases) by the indicated solvent. Table 3.1 contains data derived at a temperature of 400 C and a reaction time of 0.5 hr. Among the control solvents, it can be seen that the naphthalene and decalin give similar results and are both much less effective than tetralin, the yields of each of hexane-, benzene-, and pyridine-solubles obtained with the former being roughly half of those obtained with the latter. The greater effectiveness of tetralin as a donor-solvent relative to naphthalene and decalin is in agreement with previous studies (2,7,9). Further, the absolute conversion to benzene-solubles (plus gases) obtained with tetralin in the present work, namely 44 weight percent, compares favorably with the values of 36 and 47 weight percent reported by Neavel (9) for comparable HVA and HVB bituminous coals at similar reaction conditions. The accord between the control solvent liquefaction data shown in Table 3.1 and the literature permits us to place some confidence in the present experimental procedures. Turning now to the dialin donors, for which coal liquefaction data have not hitherto been reported, it can be seen from Table 3.1 that, relative to tetralin, the Δ^1 -dialin yielded appreciably more hexane-solubles, somewhat less benzene-solubles, and approximately the same pyridine-solubles. Also relative to tetralin, the Δ^2 -dialin yielded appreciably more hexane-solubles, approximately the same benzene-solubles, and appreciably more pyridine-solubles. It is apparent that the dialins, especially the Δ^2 -dialin, were more effective donor solvents than tetralin in liquefaction of the present coal sample. While no precise chemical interpretation can be attached to the quantities used to measure liquefaction, the pyridine-solubles roughly represent the extent to which the coal substrate is converted, whereas the hexane-solubles are a measure of the final, oil, product (the benzene-solubles represent an intermediate). Accordingly, from Table 3.1, the Δ^2 -dialin increased

the coal conversion by 16 percent and product oil formation by 37 percent relative to tetralin. A few liquefaction experiments were also conducted at a temperature of 300 C and a reaction time of 0.5 hr, with results reported in Table 3.2. Of the control solvents, decalin yielded neither hexane- nor benzene-solubles, while tetralin yielded no hexane-solubles but did yield the indicated small amounts of benzene- and pyridine-solubles. The Δ^2 -dialin yielded no hexane-solubles but provided appreciable amounts of benzene- and pyridine-solubles. The conversions seen in Table 3.2 are all much lower than the corresponding conversions in Table 3.1, undoubtedly a consequence of the lower reaction temperature, 300 C versus 400 C, reaction times being equal. Finally, Table 3.2 shows that the Δ^2 -dialin solvent produced 3 times the benzene-solubles and 5 times the pyridine-solubles produced by tetralin, a striking re-inforcement of the indication from Table 3.1 that the dialins were the more effective donors.

A second series of liquefaction experiments were conducted to test the theoretical suggestion that a mixture of Δ^1 - plus Δ^2 -dialin isomers might be a more effective solvent than either one of the dialins alone. Preliminary results at 400 C and 0.5 hr reaction time, are shown in Table 4 which quotes the ratio of the conversion to each of hexane-, benzene-, and pyridine-solubles obtained with a solvent mixture containing equal amounts of Δ^1 - and Δ^2 -dialins relative to the average of the corresponding conversions obtained with each of the Δ^1 -dialin and Δ^2 -dialin solvents separately. (Generally, if P_{MX} was the conversion to say, pyridine-solubles obtained with a solvent mixture containing a fraction x of solvent 1, while p_1 and p_2 were the conversions respectively obtained with the pure solvents 1 and 2 separately, then the departure of the ratio $r_x = P_{MX}/(xp_1 + (1-x)p_2)$ from unity will evidently measure the effectiveness of the solvent mixture relative to the separate pure solvents.) In Table 4 it can be seen that the coal conversion to hexane-, benzene-, and pyridine-solubles with the dialin mixture was respectively 28, 1, and 18 percent greater than the average for the separate solvents. These results are evidently in accord with the theoretical prediction, but further work is being undertaken to seek the generality of this result and to discern an optimum solvent mixture.

4. CONCLUSIONS

At typical coal liquefaction conditions, namely temperatures from 300 to 400 C and reaction times on the order of 1 hr, hydrogen transfer from model C10 donors, the Δ^1 - and Δ^2 -dialins, to model C14 acceptors, anthracene and phenanthrene, occurs in the sense allowed by the Woodward-Hoffman rules for supra-supra group transfer reactions. Thus, in the conversion of the C14 substrates to their 9,10 dihydro derivatives the dialins exhibited a striking reversal of donor activity, the Δ^1 -dialin causing about twice as much conversion of phenanthrene but only one-tenth as much conversion of anthracene as did Δ^2 -dialin.

The dialins were also found to be more effective donor solvents than tetralin in the liquefaction of an Illinois No. 6 HVA bituminous coal. For example, at 400 C and 0.5 hr reaction time, Δ^2 -dialin yielded 16% more pyridine-solubles and 37% more hexane-solubles than tetralin; at 300 C and 0.5 hr reaction time, the Δ^2 -dialin yielded 5 times the pyridine-solubles and 3 times the benzene-solubles yielded by tetralin.

Finally, a mixture containing equal parts of Δ^1 - and Δ^2 -dialin was found to be a more effective donor solvent than either of the Δ^1 - or Δ^2 -dialins separately. At 400 C and 0.5 hr reaction time, the mixture of donors yielded 18% more pyridine-solubles and 28% more hexane-solubles than the average for the separate donors.

The preceding experiments offer preliminary support to our notion that pericyclic pathways might be intimately involved in the mechanism of coal liquefaction. More specifically, the results indicate that pericyclic group transfer reactions constitute a plausible pathway for the transfer of hydrogen from donor solvents to coal during liquefaction.

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18. Our coal sample was obtained from Inland Steel Company Research Laboratories, Chicago, Ill. through the courtesy of Professor J.B. Howard of the Department of Chemical Engineering, M.I.T., Cambridge, Mass.

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TABLE 1.1 Model Compound Experimental Grid

Coal Model C14		
Solvent C10	Supra-Supra Allowedness	
		
		
	x	✓
	✓	x

TABLE 1.2 Model Compound Experimental Results

Reaction Conditions	Temp = 300 C Time = 2 Hr	Temp = 400 C Time = 2 Hr
Coal Model C14		
Solvent C10	% conversion to 9,10-dihydro-derivative	
	0	0
	3	2
	5	16
	58	10

TABLE 2. Coal Sample Characterization

Origin: Illinois No. 6 from Sesser, Illinois
 Rank: Bituminous, High Volatile A

Proximate Analysis: (wt% dry basis)	VM	FC	Ash	Total		
	37.3	56.7	6.0	100.0		
Elemental Analysis: (wt% daf)	H	C	N	O	S	Total
	5.4	82.0	1.6	10.2	0.8	100.0

TABLE 3. Coal Liquefaction Results

1. Temperature = 400 C : Reaction Time = 0.5 hr

Solvent	Coal Conversions to Hexane- Benzene- Pyridine- Solubles (plus gas), wt%		
	Hexane- Solubles	Benzene- Solubles	Pyridine- Solubles
Naphthalene 	8.0	-	29.7
Decalin 	10.8	22.5±2.6	32.5
Tetralin 	20.9	43.9±1.4	70.2
Δ^1 -Dialin 	27.0	39.6±1.9	71.3
Δ^2 -Dialin 	28.6	44.9±1.5	81.4

2. Temperature = 300 C : Reaction Time = 0.5 hr

Decalin 	0	0	-
Tetralin 	0	2.4±0.6	3.7
Δ^2 -Dialin 	0	9.0±1.5	19.3

TABLE 4. Coal Liquefaction by Mixed Dialin Solvent

Temperature = 400 C : Reaction Time = 0.5 hr

Solvent: 1:1 mixture of Δ^1 - and Δ^2 -dialins

Conversion Ratio r	Hexane- Benzene- Pyridine- Solubles Solubles Solubles		
	Hexane- Solubles	Benzene- Solubles	Pyridine- Solubles
	1.28	1.01	1.18

Note: $r = p_m / 0.5(p_1 + p_2)$ where p_m , p_1 , p_2 are respectively the wt% conversions obtained with mixed solvent, Δ^1 -dialin and Δ^2 -dialin.

Fig. 2. FRONTIER ORBITAL ENERGY LEVELS FOR THE REACTION OF H_2 AND NAPHTHALENE

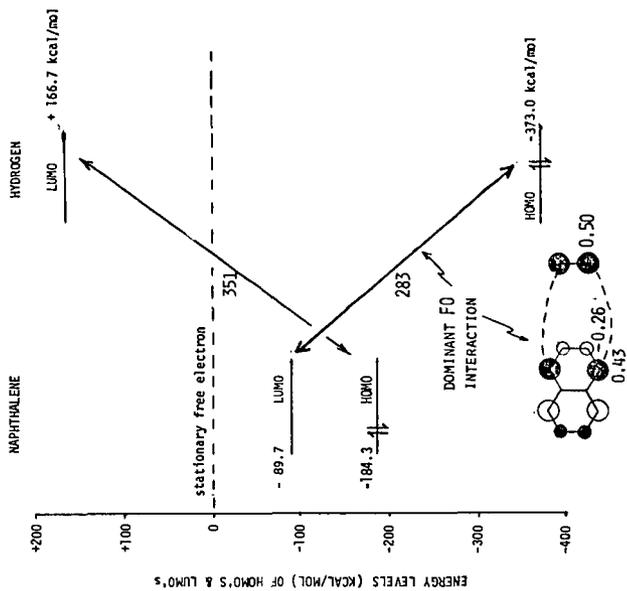


Fig. 1. SCHEMATIC REACTION PROFILE FOR GROUP TRANSFER

