

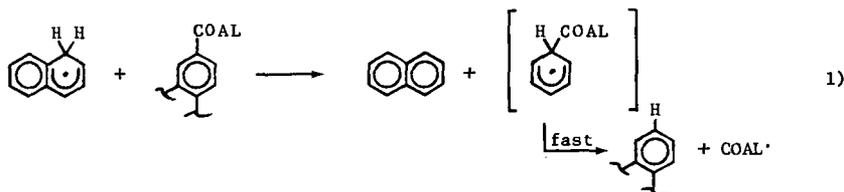
HYDROGENOLYSIS IN COAL LIQUEFACTION AND PYROLYSIS: THE RELATIVE IMPORTANCE OF SOLVENT RADICALS AND FREE HYDROGEN ATOMS

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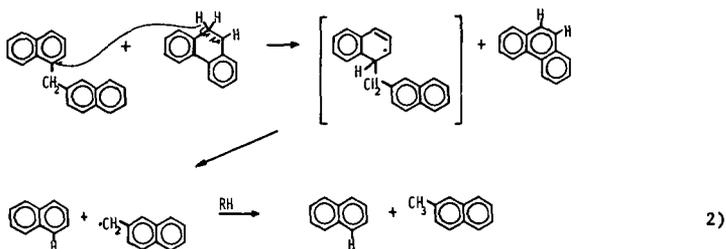
INTRODUCTION

The conventional view of coal structural fragmentation during liquefaction and pyrolysis has for many years been that those bonds in the coal structure that are weak enough, simply undergo scission in a purely thermal manner. In this view, the relative effectiveness of the various process conditions is necessarily determined by the extent to which these conditions prevent the thermally generated radicals from recombining or undergoing other "retrograde" reactions. Despite recent suggestions by several different groups that the traditional thermal-bond-scission-radical-capping mechanism is inadequate to explain the phenomenology of donor-solvent coal liquefaction (1-6), this model continues to retain its position as the most widely invoked explanation of coal-structure degradation during liquefaction. Furthermore, in those cases where it is recognized that cleavage of coal linkages includes processes that are not spontaneous thermal cleavages, but are actually engendered by the solvent system, this promoted cleavage is usually attributed solely to cracking by free hydrogen atoms (7,8). In this paper we wish to further support our contention (1,2) that a significant part of the structural fragmentation occurring during coal liquefaction is not "spontaneous", but results from a previously undocumented fundamental reaction, "radical-hydrogen-transfer" (RHT), to aromatic positions bearing aliphatic (or ether) linkages in the coal structures (reaction 1).



It is no longer at issue whether alternatives to thermal scission of inherently weak bonds exist under donor solvent coal liquefaction conditions: The observed cleavage (1,5,7) of very strong alkyl-aryl bonds in hydroaromatic media, at 400°C, in the absence of H<sub>2</sub> pressure, on coal liquefaction time scales, (reaction 2) has demonstrated that what are formally defined as hydrogenolyses do take place under conditions where free hydrogen atoms have been thought to be unimportant. The fundamentally intriguing and possibly technologically important question that remains is whether or not this cleavage simply involves the ipso addition of free hydrogen atoms, and if does not, then by what mechanism does it take place.

In order to help answer the above question, we wish to present results that (1) demonstrate the relative importance of free hydrogen atoms and solvent "hydrogen-carrier radicals" for bond scission in the donor solvent system most



Bond cleavage half-life at 400°C  $\approx$  20h

likely (of those systems generally studied) to generate "free" hydrogen atoms, and (2) suggest the relative importance of the two transfer modes for solvent systems that are much less likely to generate free hydrogen atoms (and not coincidentally are better coal liquefaction solvents).

#### EXPERIMENTAL PROCEDURE

Dihydroanthracene, 9,10-dihydrophenanthrene, tetralin, pyrene and 1- and 2-methylnaphthalene were obtained from Aldrich, and 1,2'-dinaphthylmethane was obtained from Carnegie-Mellon University. All were used without further purification. 4,5-Dihydropyrene was prepared by the procedure of Friedman et al. (8).

Model compounds reactions were conducted in sealed, 4-mm-od, fused silica ampoules that were loaded, together with some solvent (to equalize pressure), into a 3/8-in. od, Swagelok-capped stainless steel jacket. This assembly was heated in a molten salt bath temperature controlled to  $\pm 0.5^\circ\text{C}$  for the prescribed reaction time, and then quenched in a water bath. Product mixtures were analyzed by GC, and when necessary, by GC/MS.

#### RESULTS

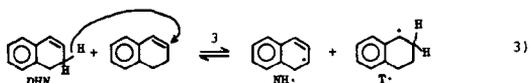
##### The Use of 1,2-Dihydronaphthalene Disproportionation Stoichiometry to Determine the Mode of Hydrogen Transfer

1,2-Dihydronaphthalene and its rapid disproportionation at 400°C to naphthalene and tetralin provides a unique opportunity to study the mechanism by which hydrogen atoms are transferred among the various hydronaphthalene structures. Since hydrogen transfer by either radical hydrogen transfer or free hydrogen atoms can result in the same products, distinction between the two modes in many other systems must be by inferences drawn from kinetic measurements through numerical modeling. However, in the case of dihydronaphthalene, determination of the naphthalene/tetralin product ratio as a function of dilution with an inert solvent provides an internal measure of the fraction of hydrogen transfers that occurs by radical hydrogen transfer and the fraction that occurs by addition of free hydrogen atoms. The disproportionation of 1,2-dihydronaphthalene is known to occur by a radical chain process initiated by a molecule induced homolysis (or reverse radical-disproportionation (5,9,10)), with the only uncertain reaction

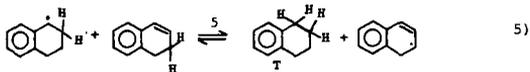
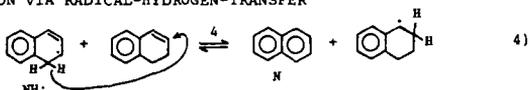
being the hydrogen transfer step that is the subject of this paper. The result of competition between transfer via free hydrogen atoms and direct bimolecular transfer from a radical carrier can be seen by inspection of the alternative reaction sequences.

DISPROPORTIONATION OF 1,2-DIHYDRONAPHTHALENE

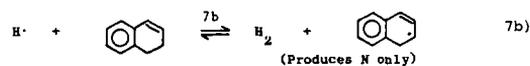
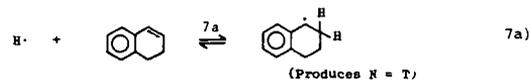
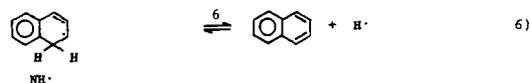
INITIATION/TERMINATION



PROPAGATION VIA RADICAL-HYDROGEN-TRANSFER



PROPAGATION VIA FREE H·



To the extent that disproportionation proceeds by way of the propagation steps 4 and 5, the ratio of naphthalene/tetralin will be identically equal to 1.0. However, to the extent that unimolecular hydrogen-atom elimination (reaction 6) from the 1-hydronaphthyl radical (1-NH·) competes with bimolecular radical-hydrogen-transfer (reaction 4), the free hydrogen atoms thus produced can either add to or abstract from DHN (reactions 7a and 7b, respectively). H-atom addition results in equal quantities of naphthalene and tetralin, just as does radical-hydrogen-transfer (reaction 4), but abstraction produces H<sub>2</sub> and naphthalene with no production of tetralin. The naphthalene/tetralin product ratio (N/T) is determined both by the ratio of radical-hydrogen-transfer/elimination and by the fraction of those free hydrogen atoms produced that go on to add to DHN rather than abstracting from it. Therefore, measurement of the change in N/T as a function of dilution with an inert solvent (one that hydrogen atoms cannot readily add to or abstract from, such as biphenyl) provides a determination of both of these branching ratios.

The steady-state algebra for this determination is simplest if we restrict consideration to initial reaction rates of a system that is far from equilibrium (i.e. DHN/N, DHN/T > 1). In that case we need to consider only the forward reac-

tions of the various propagation steps, and find the naphthalene/tetralin production ratio given by equation (8).

$$\frac{N}{T} \sim \frac{d[N]}{d[T]} = \frac{\frac{k_4 [\text{DHN}]}{k_6} + 1}{\frac{k_4 [\text{DHN}]}{k_6} + \frac{k_{7a}}{k_{7a} + k_{7b}}} \quad \left. \vphantom{\frac{d[N]}{d[T]}} \right\} F \quad (8)$$

In Figure 1 is plotted a set of curves that correspond to the relationship described by equation 8 between the ratio of naphthalene production rate to tetralin production rate and the extent of DHN dilution. Each curve is for a given value of "F," the fraction of those free hydrogens produced that go on to add to DHN.

Inspection of the general form of these curves shows it to be intuitively reasonable. Consider first, movement along the abscissa of Figure 1: for a given fraction of free hydrogen atoms that add (F fixed), the more the DHN is diluted, the more NH' will be diverted from the bimolecular RHT process (reaction 4) to the unimolecular H-elimination process (reaction 6), and the greater will be the excess of naphthalene that results from H abstraction (reaction 7b). The result of movement from one value of F to another is also reasonable: for a given DHN concentration, the lower the fraction of H that add (and therefore, the higher the fraction that abstract), the greater will be the excess of naphthalene. In the limit of no addition (F = 0), as (DHN) → 0, N/T → ∞. On the other hand, in the limit where all free H' add (and none abstract), the final result will not depend on the branching between RHT and elimination: N/T will be 1.0 at all levels of DHN dilution, as shown for the bottom curve in Figure 1. In the limits where the bimolecular transfer to elimination ratio (k<sub>4</sub>/k<sub>6</sub>) is very high or very low, either RHT or elimination of hydrogen atoms will dominate at all practical levels of (DHN), and the observed (N/T) will not vary with DHN concentration. In other words, equation 8 is useful only when radical hydrogen transfer and elimination are competitive, and when addition is not the exclusive pathway for free H-atoms.

Also shown in Figure 1 are points corresponding to measured N/T ratios in a series of experiments performed at 385°C for initial concentrations of DHN in biphenyl ranging from 2 to 30 m%. The data clearly can be well fitted to the functional form of equation 8. The best fit corresponds to a value of 1.08 l/m for k<sub>4</sub>/k<sub>6</sub>, and 0.68 for F. This means that of every 100 NH' formed, (1.08/2.08)100, or 52, will transfer their hydrogen bimolecularly (at 1.0 M concentration of the acceptor DHN), and 48 will eliminate a hydrogen atom. Of the 48 free hydrogen atoms, 68%, or a total of 33, will add, and 15 will abstract. This means that 52 out of 85 hydrogen transfers proceed through the direct bimolecular process. Thus these results are consistent with the results of Franz and co-workers (5), who reported that the hydrogenolysis of diphenylmethane in this system was, under similar conditions, always accompanied by at least some H<sub>2</sub> formation, and therefore could not be used as unequivocal qualitative evidence for operation of an RHT mechanism. In the present case, the measured effects of dilution and algebraic separation presented above provide, within the accuracy and precision limits of the data, an unequivocal determination of the relative importance of radical-hydrogen-transfer and free hydrogen atom addition.

#### Implications of Solvent-Radical-Mediated-Hydrogen-Transfer

One may question how relevant the above branching is for hydrogen transfer in coal liquefaction, where the potential recipients in the coal structure may be present at effective concentrations much less than 1 M. While it is true that in



hydroaromatic content in the solvent. Since this trend is counter to that observed in actual coal liquefaction, the mode of cleavage observed by Vernon would appear not to be representative of the bulk of the coal structure cleavage obtained in solvents of high donor content.

#### Accuracy of the RHT/Elimination Determination

Given the limited range of observed N/T ratios in Figure 1, it is appropriate to ask how precise the present determination of the radical-hydrogen-transfer/elimination ratio actually is. The two most important qualifications are that equation 8 is a differential expression, derived for initial conditions where the only important propagation reactions are 4, 5, 7a and 7b, and the reverse of these reactions can be neglected. Furthermore, the assumption is that side reactions are relatively unimportant. The first criterion is met by measuring product ratios in the initial stage of the reaction when the system is far from equilibrium. The latter criterion is marginally satisfied by choosing reaction conditions that are a compromise between excessive free hydrogen atom elimination (favored by high temperatures), and excessive formation of dimeric DHN products (favored by low temperatures and high DHN concentrations(5)). This choice provides a fairly narrow window in which to make measurements, and coupling product formation could not be completely avoided. However, for all but the point at the highest DHN concentration (30 m%), the amount of DHN coupling product formation was less than about 10%. The effect of this minor amount of coupling product on the derived branching ratios is assessed below.

Examination of the DHN coupling products identified in the thorough study by Franz and co-workers (5) indicates that these products are formed primarily, but not exclusively, at the expense of tetralin formation. If we make even the extreme assumption that the coupling products observed in our experiments were formed exclusively at the expense of tetralin, and correct the observed N/T ratios accordingly, the value of F remains essentially unchanged, and the value of RHT/elimination increases by about 30%. Thus, inaccuracies due to formation of coupling products in side reactions cannot invalidate the general conclusion that the hydrogen carrier radical in tetralin/naphthalene systems (the 1-NH<sup>•</sup> radical) transfers hydrogen bimolecularly to dihydronaphthalene at rates competitive with transfer by free hydrogen atoms.

#### Importance of Radical Hydrogen Transfer in Other Solvent Systems

The results above demonstrate that in the radical chain disproportionation of 1,2-dihydronaphthalene, hydrogen is transferred from a solvent radical to another olefinic or aromatic system, in a bimolecular reaction that was, until this work (1,2), without precedent in the chemical literature. Now one obvious question is, "How important is this reaction under conditions that more closely mimic those in donor solvent coal liquefaction?" In order to help answer this question, we have studied the cleavage of a very strongly bonded model compound in a number of donor solvent systems. At 400°C in common donor solvent systems, 1,2'-dinaphthylmethane (DNM) exhibits cleavage half-lives (forming methylnaphthalenes and naphthalene) of 3 to 200 hours, as shown in reaction 2 above. This is unquestionably a "solvent-promoted" cleavage, since no cleavage (i.e. % reaction < 0.1%) can be seen in 20 hours in pure aromatic solvents ( $t_{1/2} > 10,000$  hours). In fact the ca. 85 kcal/mol strength of the central bond (14) is such that the half-life for spontaneous thermal rupture is on the order of 100-million hours (3,12). Dinaphthylmethane is somewhat harder to cleave than analogous phenanthrene derivatives would be, and much harder to cleave than similar anthracene derivatives (2,3,12,13). Of all the single methylene bridges between aromatic groups, the only one more difficult to cleave in a hydrogenolysis process than dinaphthylmethane is that in diphenylmethane. The point is that dinaphthylmethane is in all likelihood

a relatively severe test of the bond-cleaving ability of a coal liquefaction solvent system.

Because of its unsymmetrical coupling, we have with 1,2'-dinaphthylmethane not only an indicator of the hydrogen transfer activity of a solvent system, but also an indicator of the mode of transfer. Since the 1-position of naphthalene is preferred for hydrogen atom addition or transfer (by ~ 4 kcal/mol, compared to the 2-position (3,12,13) the ratio of product resulting from attack at the 1-position to that resulting from attack at the 2-position provides a measure of the selectivity of the transfer agent and therefore an indication of the nature of the transfer process.

#### Thermochemistry of Hydrogen Transfer in Selected Systems

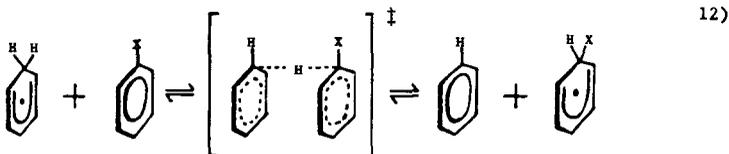
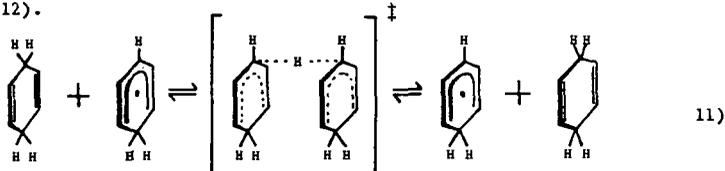
As a basis for anticipating the relative importance of radical-hydrogen-transfer (RHT) in the dihydronaphthalene system discussed above and in other solvent and acceptor systems, we need at least to know the relevant thermodynamic values. In Table 1 are given measured or estimated enthalpy (1,3,12,13) values for RHT and hydrogen atom elimination for dihydronaphthalene disproportionation (1), dinaphthylmethane cleavage in tetralin (2) and in 9,10-dihydroanthracene (3), and for 9-alkylantracene cleavage in 9,10-dihydroanthracene (4). On the basis of these values rough estimates can be made of the ratio of RHT to H<sup>•</sup> elimination.

Table 1 THERMOCHEMICAL VALUES FOR HYDROGEN TRANSFER<sup>a</sup>

System	ArH <sup>•</sup>	Ar-X	$\Delta H^\circ, \text{kcal/mol}$		est. $E_a$		$k_{\text{RHT}}(\text{ArX})/k_{\text{elim.}}$
			H <sup>•</sup> elim.	RHT	H <sup>•</sup> elim.	RHT	
1			+30	-15	31	13	(1.1)
2			+30	0	31	16	0.1
3		"	+45	+15	46	28	1.1
4	"		+45	0	46	16	10 <sup>4</sup>

<sup>a</sup>Values taken directly from, or estimated on the basis of, data in references 3,12,and13.

The ratio of the RHT rate to the H<sup>•</sup> elimination rate for the first system is in fact the ratio whose determination is discussed above. The estimation of the H<sup>•</sup> elimination rate constant is subject to relatively little uncertainty, since the intrinsic activation energy for hydrogen-atom elimination is known (14,15) to be no more than about 1 kcal/mol. The "estimated" rate constant for RHT was then adjusted to fit the measured RHT/elimination ratio by assuming that the generic A-factor for RHT (reaction 11) was 10<sup>8.5</sup> l/m-sec, a well-accepted (3,15) "representative" value for the ubiquitous and geometrically similar metathesis reaction (Reaction 12).



This adjustment resulted in an activation energy of 13 kcal/mol, not unreasonable for a 15 kcal/mol exothermic transfer, in view of measured activation energies (3,5) of about 16 kcal/mol for thermoneutral metathesis reactions involving two resonance-stabilized radicals. This adjustment provides a reasonable base for semi-quantitative speculation about the relative rates of RHT and elimination for the other three systems in Table 1.

When DNM (rather than 1,2-DHN) is the acceptor of the hydrogen, the transfer from the NH<sup>•</sup> radical is now nearly thermoneutral (assuming transfer to the aromatic naphthalene system is otherwise similar to transfer to the isolated double bond of 1,2-DHN) and one would expect a slightly higher intrinsic activation energy. This results in the expectation that RHT in system 2 may now be as much as 10X slower than elimination. In the third system, transfer from the 9-hydroanthryl radical (AnH<sup>•</sup>) to DNM is 15 kcal/mol endothermic, and elimination is about 45 kcal/mol endothermic. Assuming symmetrical behavior of the potential energy surface moving from exothermic to thermoneutral to endothermic RHT, the intrinsic activation energy would again be 13 kcal/mol (making E<sub>a</sub><sup>obs</sup> = 13 + 15 = 28 kcal/mol). The net result is to make the RHT/elimination ratio the same as case number one, where RHT was 15 kcal/mol exothermic.

The largest change in the series is expected for the fourth system. Here, for thermoneutral transfer from an anthracene carrier to an anthracene acceptor, the anticipated activation energy for RHT drops by more than 10 kcal/mol as compared to System 3, while that for H<sup>•</sup> elimination remains constant, and the RHT is expected to exceed elimination by more than three orders of magnitude. Stein and co-workers have recently completed (16) studies on one example of System No. 4 (9,10-dihydroanthracene/9-ethylanthracene) and have apparently found the kinetics of hydrogen transfer to be wholly inconsistent with hydrogen transfer by way of free hydrogen atoms, but consistent with the radical-mediated bimolecular transfer process invoked in this work. We find this agreement gratifying. However, we also note that the evidence we provide in this paper for the importance of

Radical-Hydrogen-Transfers even in the less "favored" systems, 1 and 3, is a much stronger suggestion of its widespread significance in coal liquefaction.

#### Implications for Coal Liquefaction

From the above discussion, it seems clear that the "hottest" hydrogen carrier radical is not necessarily the best for coal liquefaction. Clearly, what is desired is maximum reactivity coupled with the maximum attainable selectivity for RHT and against H-atom elimination. In general, this will be best obtained through maximum numbers of  $ArH^{\cdot}$  of reactivity low enough that H-elimination is not a substantial side reaction. This criterion is more successfully met by the tri- and tetracyclic PCAH systems than by the tetralin/naphthalene systems.

In order to determine the relative importance of RHT and free hydrogen atom addition as hydrogenolysis pathways in Systems 2 and 3 and related systems, we are using, as an indicator, the internal or positional selectivity in the cleavage of 1,2'-dinaphthylmethane. In various experiments performed thus far, in which the donor solvents have included tetralin, dihydrophenanthrene, dihydroanthracene, dihydropyrene, tetrahydroquinoline, and indoline, the fully aromatic counterparts of some of these solvents, and mixtures of the pure solvents with coals or coal products, we have observed the ratio of 2-methylnaphthalene/1-methylnaphthalene to range from about 2.2 to 4.8. Some of these data are shown in Figure 2, where the observed ratio is plotted as a function of the endothermicity of hydrogen transfer from the respective solvent radical  $ArH^{\cdot}$ .

The variation in selectivity shown in Figure 2 demonstrates, at a minimum, that the hydrogen transfer which results in the DNM cleavage is not, in all cases, due to free hydrogen atoms. The increase in selectivity as the hydrogen transfer becomes more endothermic indicates either that (1) the transfer is in all cases by an RHT process that naturally becomes more selective as the reactivity of  $ArH^{\cdot}$  decreases, or (2) that in the case of the system of least selectivity (tetralin/naphthalene), the transfer is wholly or partly via free hydrogen atoms, and that the proportion of transfer by RHT increases as the radicals  $ArH^{\cdot}$  become less reactive. In either event, these data provide unequivocal evidence that transfer via free hydrogen atoms could be the sole mode of cleavage, at most, only for the naphthalene/tetralin system.

The data in Figure 2 do not illustrate the additional fact that the 2-Me-N/1-Me-N ratio can vary not only as a function of solvent system, but also as a function of the acceptor concentration in the solvent. For instance, in the case of dihydroanthracene, the ratio varies from about 3 to about 7, depending on whether the solvent is predominantly dihydroanthracene or anthracene, respectively. This is in accord with the observation made above, namely that if a successful encounter with a cleavable coal structure is not made before the hydrogen atom is unimolecularly eliminated from the original  $ArH^{\cdot}$  carrier, a large pool of the aromatic component acts as a temporary acceptor for the hydrogen atom. Thus, for a given  $ArH^{\cdot}$  steady-state concentration, the likelihood that an acceptor will receive a hydrogen atom in an RHT process is a function not only of the acceptor concentration, but also of the Ar concentration in the solvent pool. In experiments currently underway, we are determining the cleavage product ratio as a function of DNM and Ar concentrations. If, by sufficiently disfavoring and favoring the RHT process relative to transfer via free hydrogen atoms, we can reach a single demonstrable minimum for all solvent systems and unique maxima in the 2:1-methylnaphthalene product ratios for each solvent system then we will have determined the product ratios for cleavage purely by free hydrogen atoms on the one hand and purely by RHT on the other hand. Having determined these values, the product ratios observed under other conditions will be a direct and unequivocal measure of the relative contribution of cleavage by the two hydrogen transfer modes. Such results should put us one significant step closer to the goal of understanding the chemistry by which hydrogen can be shuttled from one

position in the solvent or coal structure to engender cleavage at another position, while minimizing the requirement for high hydrogen pressures or heterogeneous catalysts. Finally, an awareness of the importance of hydrogen-transfer-promoted bond cleavage in coal liquefaction suggests that it is also important in coal pyrolysis, and that a better understanding of the process would allow it to be augmented under the conditions of pyrolysis.

#### ACKNOWLEDGEMENTS

The authors wish to acknowledge the support of the U.S. Department of Energy under contracts DE-FG22--84PC70810 and DE-AC22-81PC40785.

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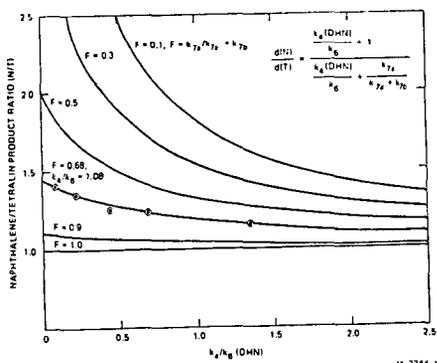


FIGURE 1 EFFECT OF DILUTION WITH BIPHENYL ON THE PRODUCT RATIO IN THE DISPROPORTIONATION OF 1,2-DIHYDRONAPHTHALENE AT 385°C

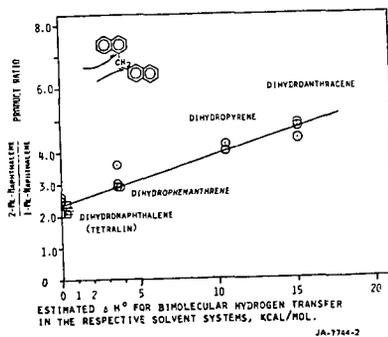


FIGURE 2 SELECTIVITY FOR HYDROGEN TRANSFER FROM SOLVENT RADICALS: RATIO OF ONE-POSITION TO TWO-POSITION TRANSFER TO DINAPHTHYLMETHANE