# MOLECULE-INDUCED HOMOLYSIS IN COAL CHEMISTRY: RADICAL INTERMEDIATES IN THE THERMAL DECOMPOSITION OF 1,2-DIHYDRONAPHTHALENE*

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Molecule-induced homolysis (MIH), the process by which two closed-shell molecules react to produce free radicals, has been recognized as an important contributing pathway to radical initiation during coal dissolution(1,2). The production of organic radicals by MIH and other pathways can lead in stepwise fashion to the production of highly reactive radicals to a significant degree at temperatures >400°C. In this paper, we summarize results which show that the decomposition of 1,2-dihydronaphthalene (DHN) involves both 1-hydronaphthyl (1HN) and 2-hydronaphthyl (2HN) radicals as well as 1-tetralyl radical and that the production of 1HN and 2HN leads to the scission of hydrogen atom (H•) and its participation in subsequent hydrocracking reactions.

Experimental. 1,2-Dihydronaphthalene (Aldrich) was purified by careful fractional distillation. 1,2-Dihydro-4-deuteronaphthalene(DHN-4-d) was prepared by treatment of 1-tetralone with lithium aluminum tetradeuteride. The 1-deuterotetralol (21g) was heated at 100°C for 20 minutes at reduced pressure with $KHSO_4$ (2g) followed by flash distillation. The crude product was dissolved in hexane, filtered through neutral alumina, and concentrated to give pure ( 99.7%) product in 66% overall yield. Thermal decomposition of DHN or DHN-4-d was carried out by degassing and sealing the reagents in pyrex tubes and placing the tubes in stainless steel vessels and surrounding the pyrex tubes with tetralin to balance internal pressure. Yields of products, naphthalene, tetralin and $C_{20}$ compounds were measured by capillary gas chromatography (gc). The $C_{20}$ products, 1-5 (Figure 1), were isolated from 16 hour reactions at 300°C by preparative gc and characterized by $^{13}C$ NMR (20 MHz) and $^{1}H$ NMR (300 MHz) and mass spectrometry for both DHN and DHN-4-d precursors. Compound 2 was subjected to an exchange of its benzylic hydrogen by heating in sodium dimsylate-$d_5$/DMSD-$d_6$ at 100°C. Reactions of DHN and the reagents of Table 1 were carried out at 425°C for 10 minutes and the product mixtures were analyzed by capillary gc for hydrocracked products. Products were identified by coinjection of authentic standards.

## Results

Products of the thermolysis of DHN. When DHN is heated at 300°C the products, tetralin (40 ± 10%), naphthalene (40 ± 10%), $C_{20}$ compounds, 1-5, (15% combined yield) and a variety of trace ( 5%) $C_{20}$ products are formed. When heated at 425°C, $C_{20}$ compounds comprise less than 5% of the products, naphthalene is formed in excess of tetralin and $H_2$ gas is formed.

Structures of Compounds 1-5. Compounds 1 and 2 each exhibited molecular weights of 260, four aliphatic methine carbons, 4 aliphatic methylene carbons,

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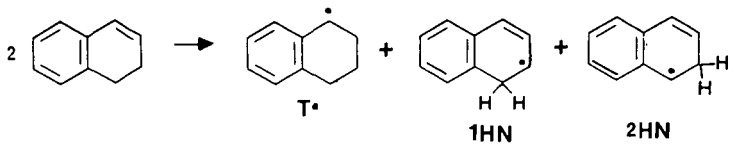
4 unprotonated aromatic carbons along with the protonated aromatic carbons as determined by off-resonance decoupling techniques. $^1$H NMR at 300 MHz revealed 12 fully resolved aliphatic hydrogens for each of 1 and 2. Compounds 3, 4, and 5 exhibited molecular weights of 262, 262 and 258. Homonuclear decoupling unambiguously established the structure of 1, as well as establishing the syn relationship of hydrogens b and h shown in the structure of 2. Deuterium exchange with compound 2 removed protons a, b, c, f, and g, but not d. When DHN-4-d was used to produce isomers 1-5, deuterium appeared only as shown in the product structures.

Hydrocracking Reactions. Table 1 presents hydrocracking reactants and products. The modest yields of products reflect the large number of competing reactions which consume H• and do not produce hydrocracked products.

## Discussion

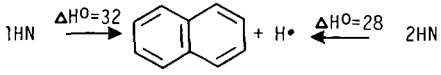
The principle initiation pathway for the DHN reaction is proposed to be that of Equation 1. The value of $\Delta H_f^o{}_{298}$ for 1HN assumes a DH$^o$ for the 3-hydrogen




(1)

| | | | | |
|---|---|---|---|---|
| $\Delta H^o_{f,298}$ kcal/mole | 30 | 35 | 56 | 60 |

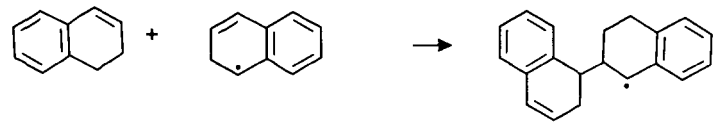
of DHN to be 94.5 kcal/mole corrected for the difference in resonance stabilization energy (ΔRSE) between DHN and 1HN (ΔRSE), 16.7 kcal/mole, from Herndon's calculations (3). The value for 2HN assumes no resonance stabilization of DHN by the styrene-like olefinic portion of the molecule, giving a value of RSE of 12.4. Thus, the value of $\Delta H^{\neq}$ for reaction of the two molecules of DHN to give 1-tetralyl (T•) and 1HN is 31 kcal/mole, and 35 kcal/mole to produce T• and 2HN•. Other thermochemical values in Equations 1 and 2 are experimental values or estimates (4). Thus, appreciable concentrations of both 1HN and 2HN are expected at 300$^o$C and above. Both 1HN and 2HN may undergo elimination of H• (Equation 2) with activation barriers of 30-35 kcal/mole, assuming 2-3 kcal barriers for H• addition to naphthalene.



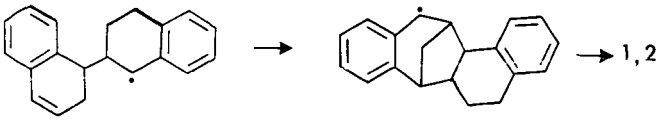

(2)

The structures of 1 and 2 are both consistent with the addition of 2HN to DHN followed by a second internal cyclization step and hydrogen abstraction from available donors (Equations 3, 4).

Both compounds 1 and 2 arise from face-to-face interaction of DHN and 2HN. The different products arise from the two different possible orientations of DHN in Equation 3. When DHN-4-d is used to produce 1 and 2, deuterium is predicted to occur at one methine and one methylene carbon, as observed. For possible structures arising from 1HN, two adjacent methine carbons would have been deuterated.

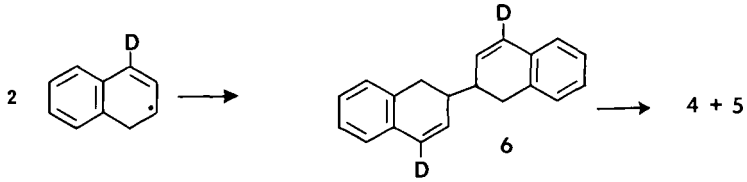


(3)



(4)

Compound 4, when produced from DHN-4-d, has deuterium solely at the position indicated. This dictates that 4 is derived from the symmetrical termination product of 1-HN which has undergone further reduction (Equation 5), as opposed to



(5)

a pathway involving the adduct of 1HN to DHN, which would lead to 2 deuterated aliphatic carbons (only one deuterated methylene is observed). If intermediate 6 undergoes a net disproportionation, compound 5 is produced. Compound 3 arises from either the termination of T• and 1HN followed by reduction or the addition of T• to DHN followed by H• abstraction. Thus, these products provide convincing evidence that 1-tetralyl, 1-hydronaphthyl, and 2-hydronaphthyl radicals are important intermediates in the decomposition of DHN, consistent with the MIH pathway of Equation 1. It was previously established by Heesing and Muller (5) that the primary products, tetralin and naphthalene, were produced in a non-concerted reaction, but the intermediacy of 1HN and 2HN was not established because the structures of $C_{20}$ products were not determined. Both 1HN and 2HN can of course be produced by H• abstraction from DHN.

At higher temperatures (>400°C), $C_{20}$ products are insignificant and $H_2$ is formed in significant (10-30%) yields. The products of Table 2 are best explained by addition of H• (compare Benson's study of cyclohexadiene (6)) at the ipso position of the aryl group followed by departure of the substituent radical. The source of H• must be the elimination of H• from radicals such as 1HN and 2HN with modest barriers of 30-35 kcal/mole. Thus, the process of molecule-induced homolysis which occurs between structures which are relatively easily oxidized or reduced, together with chain decomposition steps, leads ultimately to hydrogen atoms, with no intermediate step requiring more than 35 kcal/mole. Partially oxidized or reduced structures in coal, or compounds capable of exceptionally stable radicals thus probably play an essential role in initiation pathways during coal dissolution leading ultimately to the cleavage of strong C-C bonds.

Table 1. Thermolysis of 1,2-Dihydronaphthalene in the Presence of Other Compounds.

| Reagent (wt., mg) | DHN (wt., mg) | Products (% yield)[a] |
|---|---|---|
| Phenylether (450) | 82 | Phenol (1.4%) |
| Diphenylmethane (207) | 35 | Toluene (2.6%) |
| Tetralin (92) | 13 | n-butylbenzene (5.1%) |
| 2,6-Dimethylnaphthalene (74) | 24 | 2-methylnaphthalene (2.6%) |

[a] Mole produced per mole DHN consumed.

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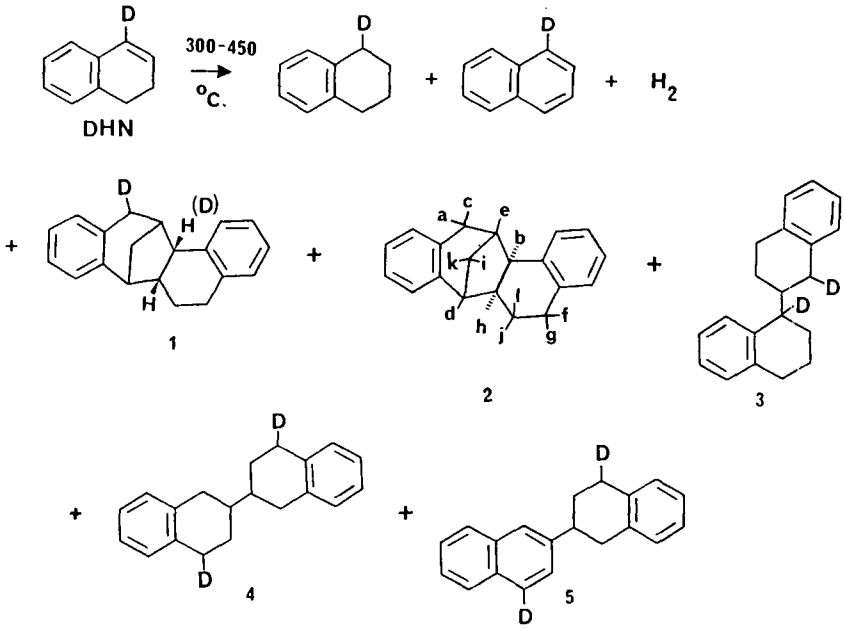


Figure 1. Major Products from the Thermal Decomposition of DHN. Deuterium atoms indicate label positions when DHN-4-d was used.