

PROMOTION OF DEUTERIUM INCORPORATION FROM D₂ INTO
COAL MODEL COMPOUNDS BY BENZYLIC RADICALS

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INTRODUCTION

A large number of revealing mechanistic investigations have been carried out dealing with the thermolysis of coal and compounds which model its structure. Perhaps because of experimental difficulties, much less attention has been given to the reaction with molecular hydrogen. It seems fair to say that the detailed mechanism by which molecular hydrogen, separately or in combination with "donor solvents", is able to effect the reductive simplification of coal is not completely understood. An obvious approach to following the reaction with H₂ is to substitute D₂. The literature contains ample evidence that deuterium is incorporated into reaction products when thermolysis of coal and coal models is carried out under D₂ gas.¹ It has also been shown that D-labeled substrates, such as tetralin-d₁₂, transfer D atoms back to dihydrogen such that HD is produced from H₂.²

Similarly it is clear that once incorporated into a molecule of organic substrate, transfer of D atoms between molecules is often facile.³ Several mechanisms can be involved in the scrambling process. Molecule-induced homolysis and symmetry-allowed, pericyclic mechanisms have been documented by Brower and Pajak.⁴ A demonstration of radical-promoted exchange was provided by King and Stock⁵ who showed that the presence of species which undergo facile homolysis increases the rate of transfer of deuterium between benzylic positions in different molecules. The mechanisms suggested seem reasonable, however, most of the proposed schemes do not address the question of how the initial transfer from H₂ occurs.

The facility of the scrambling reactions makes the question of how the hydrogen is transferred from H₂ gas into the coal structure in the first place, a particularly difficult one to answer because the initial landing site of the hydrogen atoms is rendered uncertain. Because the H-H bond is quite strong, this initial step would seem likely to be a major obstacle to the process of interest and slower than subsequent events. A scheme put forward by Vernon⁶ proposes hydrogen abstraction from H₂ by benzyl-type radicals. This suggestion was later supported by Shin.⁷ Vernon's suggestion is based on the observation that the cleavage of 1,2-diphenylethane, DPE, gives an increased yield of benzene when the reaction is carried out under H₂. The phenomenon is more pronounced when the reactions are run in the absence of a hydrogen atom donor (tetralin or 9,10-dihydrophenanthrene). It is suggested that benzyl radicals react with dihydrogen, producing toluene and

hydrogen atoms. The hydrogen atoms thus generated are responsible for the hydrogenolysis of the DPE to give benzene. In the presence of hydrogen donor solvents, the benzyl radicals react to give toluene and the production of H atoms is reduced. The latter part of this scheme seems quite reasonable based on the observed facility of reaction between benzyl radicals and compounds with structures similar to donor solvents.⁸ Likewise, the reaction of hydrogen atoms with the aromatic ring of DPE seems reasonable both on energetic grounds and in consideration of the results of Price⁹ who showed that H-atoms generated in the thermolysis of toluene above 500 °C react with toluene to produce CH₃ and H₂ with nearly equal rates. The reaction between benzyl radicals and H₂ seems the most uncertain part of the scheme in that the C-H bond energy of toluene is 85 kcal/mole where as that of H-H is 104 kcal/mole.¹⁰ The reaction of benzyl radical with dihydrogen to form toluene and hydrogen atoms is thus likely to have an activation enthalpy of more than 20 kcal/mole. This would seem to make it an unlikely competitor with various other potential reactions of benzyl radicals which are possible in the system studied.

An additional uncertainty regarding these reactions, is that most of the reported exchange studies using D₂ as a source of deuterium had utilized metal reactor vessels. This raised the question of whether the initial process for introduction of D atoms into the thermolysis milieu might be metal catalyzed. Either the walls of the reaction vessel or metal species contained in common reactor vessel sealants are possible stopover points for D atoms prior to their introduction at the seminal sites for the scrambling process. If these were involved, the well-precedented process of double bond reduction by metal-bound deuterium would then be a likely entry route for D atoms. In cases where liquefaction is accomplished by the deliberate addition of hydrogenation catalysts, this would be the expected mechanism.¹¹ As we wished to understand the noncatalyzed reaction and to use it as a base line for further studies of catalytic agents, we designed and employed a suitable glass reaction vessel.

RESULTS AND DISCUSSION

Using the glass reactor vessel described in the experimental section, we have carried out the thermolysis of 1,2-diphenylethane, DPE, under 2000 psi of D₂ gas at 450 °C. DPE disappeared following a first order rate law as shown in Figure 1. The resultant mixture showed products reported earlier by Poutsma¹² for this reaction in the absence of D₂: toluene, benzene, ethylbenzene, stilbene, 1,1-diphenylethane, phenanthrene and diphenylmethane. We also found what appeared to be diphenylpropane and trace amounts of other materials. For comparison, we carried out the reaction at the same pressure of N₂ and found most of the same products except, as reported by Vernon,⁶ greatly reduced relative amounts of stilbene, benzene and ethylbenzene. These results are shown in Table I.

Representative GC/MS data on the mixture obtained from the D₂ reaction are shown in Table II. The data suggest that deuterium introduction is taking place both at aliphatic positions and in the aromatic rings (note both benzene-d₁ and -d₂ are formed.) To assess the relative amounts of aromatic and aliphatic substitution, the reaction mixture was subjected to gas chromatographic separation and the individual components analyzed by both ²H-NMR and ¹H-NMR. Typical results are shown in Table III.

Interestingly, as seen in Table II, the pattern is very similar for

deuterium distribution in toluene and DPE at low conversion. Later in the reaction, the amount of deuterium in DPE is significantly greater than in toluene. Surprisingly, despite the fact that hydrogen atoms must be supplied in order for DPE to be converted to toluene, the toluene formed at low conversions (in the 8 minute run, ca. 20% of the bibenzyl has been converted to products and about half of this is toluene) contains only about 20% of one atom of D by GC/MS. This can only mean that at least 80% of the benzyl radicals reacting to give toluene do so by removing H atoms, presumably from DPE, rather than D atoms from D₂. Moreover, the fact that at short reaction times, there is already a substantial amount of D in the starting DPE, demands that at least some of the D-substituted toluene arises because it is formed from D-substituted DPE. This strongly suggests that DPE molecules can pick up D atoms without first undergoing homolysis.

If this reasoning is correct, it suggests that the most prominent reaction of the R· + D₂ → R-D + D· type, is that in which R· = 1,2-diphenylethyl radical rather than benzyl radical. This is somewhat surprising in that more highly-substituted radicals are normally viewed as being more stable and consequently less reactive. On the other hand, in the equilibration of species present during reaction conditions, the diphenylethyl radical will achieve higher concentration¹³ which will compensate for its possibly lower reactivity. Further, results to be described later for a new substrate suggest that viewing more highly-substituted radicals as less reactive, may be an oversimplification.

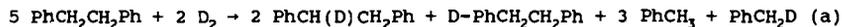
It will be noted that the deuteration pattern for ethylbenzene as seen in Tables I and II, is distinctly different from those of toluene and DPE. If, as is generally accepted,⁶ ethylbenzene is formed by the reaction of 2-phenylethyl radical with a hydrogen source, the results suggest that, being a more reactive radical, the 2-phenylethyl radical is less selective and therefore reacts directly with D₂ to a greater extent than do the more stable benzylic radicals present. Even after only 10% conversion of DPE, about 50% of the ethylbenzene molecules present contain deuterium. A similar situation exists for 1,1-diphenylethane which is believed to arise from 2,2-diphenylethyl radical, believed to be formed by rearrangement.¹² (See Table II.) Unfortunately, we have not yet been able to get reliable GC/MS data for benzene at low conversion because of the problem of getting it cleanly separated from solvent on the GC. We are still working on this.

It has been possible to isolate the more abundant products by preparative GC. We have then determined both ²H and ¹H NMR spectra using DCO₂Me as an internal standard for both spectra. This has allowed us to calculate the relative amounts of GC/MS-determined D atoms which are located at aliphatic vs aromatic sites. These data are shown in Table III for toluene, DPE and ethylbenzene. It is immediately apparent that deuterium is being incorporated at both aliphatic and aromatic sites. Moreover, the D-atom populations at the two types of location would appear to be similar in magnitude. This is consistent with a mechanism in which each aliphatic D atom introduced via R· + D₂ → R-D + D· results in D-atom incorporation in an aromatic ring. More detailed analysis of the recovered DPE suggests that the number of aromatic D atoms exceeds the number of aliphatic D atoms by a factor of between 1.2 and 1.5 (average = 1.4). This would suggest that there is some mechanism for D incorporation at aromatic sites which does not require an aliphatic radical precursor. There are a variety of possibilities, but one of the simplest is the displacement of H atoms by D atoms (probably a two step process such as reactions 4 and 9 in Figure 3). The H atoms thus generated could then react with

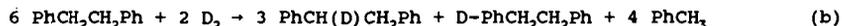
D₂ to generate more D atoms. It is reasonable to expect that if D atoms can displace alkyl radicals from the aromatic ring, the same can happen for H atoms with a five to one statistical advantage. Seeing that the amount of ethylbenzene produced is roughly 10% of the total conversion, it is perhaps reasonable to find a substantial excess of D at aromatic sites.

By computer simulation, we have tried to match the product distribution (including deuterated products) using only the first 8 reactions shown in Figure 3. These account only for the introduction of deuterium into starting DPE and the formation of toluene. We felt if we could get close to an accommodation of the data with this simple scheme, we could then approach the full set of products by elaboration and fine tuning. It will be noticed that the reaction of benzyl radicals with molecular deuterium ($\text{PhCH}_2\cdot + \text{D}_2 \rightarrow \text{PhCH}_2\text{D} + \text{D}\cdot$) has been omitted.

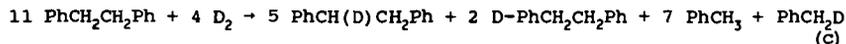
The assumption that only the reactions 1 through 8 are involved leads to the conclusion that the stoichiometry for formation of the major products should be between:



and

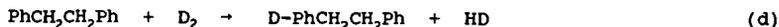


Eq (b) represents the limit in which reaction 2 (Figure 3) becomes so preferred relative to reactions 7 and 8 that all of the toluene formed arises via reaction 2 and thus would contain no D. Eq (a) results from the limit wherein reactions 5 and 6 become unimportant relative to reaction 3 thus maximizing the amount of PhCH₂D produced. If reactions 5, 6, 7 and 8 all participate equally in consuming the adduct, then the intermediate stoichiometry of eq (c) should be found.



Clearly none of these options nor any gradation in between can explain the observed facts. The observed ratio of PhCH₂D and PhCH₃ is not far from the stoichiometry of eq (c), but the experimentally observed ratio of aromatically deuterated DPE to aliphatically deuterated DPE is found experimentally to be rather constant at a value of 1.4. The stoichiometries of eqs (a), (b), or (c) demand that the ratio be between 0.25 and 0.40. Even if a huge isotope effect were assumed favoring reaction 5 over reaction 6, the maximum possible ratio would be 1.0.

Reactions 9 and 10 coupled with reaction 4, constitute a kinetic chain sequence for the introduction of aromatic D without producing aliphatically deuterated DPE. The stoichiometry of this sequence, taken in isolation from the other reactions is simply:



It therefore seems that it should be possible to combine reactions 1 through 10 to approximately match the experimental data by selecting an appropriate set of relative rates. We are working on this proposition at the present time and preliminary results indicate that it will be possible to match the distribution of the major products.

EXPERIMENTAL SECTION

Reaction Procedure. The device shown in Figure 2 (a) consists of a thick glass reaction bulb with a long capillary neck. The reactor is inverted and several glass beads are added followed by solid reactants through the end opposite to the capillary. The reactor is sealed at the constriction Figure 2 (b). The vessel is then suspended in glass wool in the interior of a stainless steel reaction tube having a long neck to house the capillary section of the vessel. The entire apparatus is evacuated, pressured with D₂ gas, closed off and shaken at the desired temperature in a fluidized sand bath. When the reaction is complete, carbon disulfide is added and products removed for analysis using a long syringe needle. In the absence of gas generation within the tube, our observation has been that little or no material is lost from the interior of the bulb. Control experiments in which a hydrogenation catalyst was deliberately added showed complete saturation of aromatic compounds under the reaction conditions.

REFERENCES

1. a. Skowronski, R. P.; Ratto, I. B.; Goldberg, I. B.; Heredy, L. A. Fuel **1984**, 63, 440-448. b. Ratto, J. J. ACS Fuel Chem. Preprints **1979**, 24, 155. c. Goldberg, I. B.; Crowe, H. R.; Ratto, J. J.; Skowronski, P. R.; Heredy, L. A. Fuel **1980**, 59, 133. d. Noor, N. S.; Gaines, A. F. Abbott, J. M. Fuel **1986**, 65, 67-73. e. Kershaw, J. R.; Barrass, G. Fuel **1977**, 56, 455.
2. Cronauer, D. C.; McNeil, D. C.; Ruberto, R. G. Fuel **1982**, 61, 610-619.
3. a. Franz, J. A.; Camaioni, D. M. Fuel **1984**, 63, 213-229. b. Franz, J. A. Fuel **1979**, 58 405-412. c. Aulich, T. R.; Knudson, C. L.; Hawthorne, S. B. Preprints Div. of Fuel Chem., Am. Chem. Soc. **1988**, 33, 368-379. d. Benjamin, B. M.; Douglas, E. C.; Mesmer, S. ibid. **1982**, 27, 1-5.
4. a. Pajak, J.; Brower, K. R. J. Org. Chem. **1986**, 50, 2210-2216. b. Brower, KR.; Pajak, J. ibid., **1984**, 49, 3970-3973.
5. King, H. H.; Stock, L. M. Fuel **1982**, 61, 257-264.
6. Vernon, L. W. Fuel **1980**, 59, 102.
7. Shin, S.-C.; Baldwin, R. M.; Miller, R. L. Energy and Fuels **1989**, 3, 71-76.
8. Bockrath, B.; Bittner, D.; McGrew, J. J. Am. Chem. Soc. **1984**, 106, 135-138.
9. Price, S. J. Can. J. Chem. **1962**, 40 1310.
10. Benson, S. W. J. Chem. Ed. **1965**, 42, 502.
11. a. Chien, P.-L.; Sellers, G. M.; Weller, S. W. Fuel Processing Technology **1983**, 2, 1-9. b. Brammer, S. T.; Weller, S. W. ibid. **1979**, 2, 155-159. c. Patxer, J. F.; Farrauto, R. J.; Montagna, A. A. Ind. Eng. Chem. Process Des. Dev. **1979**, 18, 625-630. d. Davis, K. P.; Garnett, J. L. J. Phys. Chem. **1971**, 75, 1175-1177. e. Davis, K. P.; Farnett, J. L.; O'Keefe, J. H. Chem. Communications **1970**, 1672-1673.

12. a. Poutsma, M. L.; Dyer, C. W. J. Org. Chem. **1982**, *42*, 4903. b. Buchanan, A. C.; Dunstan, T. S. J.; Douglas, E. C.; Poutsma, M. L. J. Am. Chem. Soc. **1986**, *108*, 7703.

13. Livingston, R.; Zeldes, H.; Conradi, M. S. J. Am. Chem. Soc. **1979**, *101*, 4312-4319.

Table I. Product Distribution in the Thermolysis of Diphenylethane at 450° C for 30 Minutes

	Mole % Under D ₂	Wt. % Under D ₂	Mole % Under N ₂	Wt% Under N ₂
1,2-Diphenylethane	23.5	36.6	36.1	47.1
Toluene	47.8	37.1	47.1	31.1
1,2,3,4-Triphenylbutane	0.25	0.8	<0.1	<0.1
Benzene	17.2	9.3	0.9	0.5
Ethylbenzene	8.6	7.7	--	--
1,1-Diphenylethane	1.5	2.3	0.9	1.2
Stilbene	1.3	1.9	12.2	15.8
Phenanthrene	0.8	1.2	<0.3	<0.5
Triphenylpropane	0.8	1.8	0.7	1.9
Diphenylpropane	0.44	0.73	--	--
Diphenylmethane	0.36	0.52	1.4	1.7

Table II. Deuterium Distribution in Products from Thermolysis of Diphenylethane at 450 °C Under D₂

Compound	After 8 min					After 30 min				
	%d ₀	%d ₁	%d ₂	%d ₃	%d ₄	%d ₀	%d ₁	%d ₂	%d ₃	%d ₄
1,2-Diphenyl-ethane	66	28	6	1	-	14	29	29	17	7
Toluene	78	20	2	-	-	45	36	14	4	1
Benzene	54	39	7	-	-	46	41	12	2	-
Ethylbenzene	42	45	12	1	-	18	34	29	14	4
1,1-Diphenyl-ethane	40	43	15	3	-	9	24	30	22	11
Stilbene	70	23	6	-	-	36	33	20	8	3
Phenanthrene						25	34	25	12	4
Diphenyl-methane	67	27	6	-	-	30	33	22	10	4

Table III. Aliphatic vs. Aromatic Deuterium in Products from Thermolysis of 1,2-Diphenylethane under D_2 at $450^\circ C$ by NMR.

Compound	Time (min)	Aromatic D /molecule	Aliphatic D	
			/molecule CH_2	CH_3
1,2-Diphenyl-ethane	8	0.13	0.09	
	30	0.91	0.65	
Toluene	8	0.17		0.18
	30	0.65		0.39
Benzene	30	0.66		
Ethylbenzene	15	0.36	0.18	0.54
	30	0.50	0.28	0.44
	45	1.32	0.54	0.71

Figure 1. First-Order Plot for Conversion of 1,2-Diphenylethane Under D_2 at $450^\circ C$.

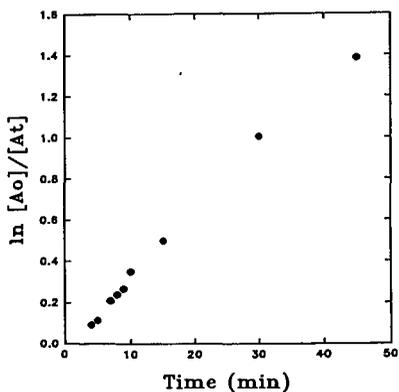


Figure 2. Glass Reaction Vessel for Thermolysis Under D_2 .

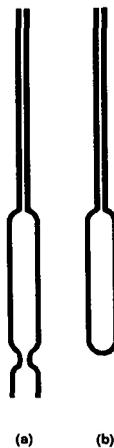


Figure 3. Minimum Steps to Explain Deuterium Distribution Pattern

