Reaction of 1,2-Diphenylethane with D_2

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The reaction of 1,2-diphenylethane (**DPE**) with D_2 (2000 psi) was studied at 450 °C. The results of GC/MS and NMR analysis of reaction products and of products from reactions of 1,2-diphenylethane-*1,1*-d_2, 1,2-di(phenyl-d_5)ethane, and 1,2,3,4-tetraphenylbutane confirm a mechanistic scheme in which the main process for introduction of D is the reaction of 1,2-diphenylethyl radical with D_2. This reaction, though energetically uphill, competes with termination processes because of the high concentration of D_2 relative to that of radical species. The reaction generates D atoms which attack aromatic ring positions to give substitution for both H and alkyl substituents. Evidence is provided for D and H atom transfer between aliphatic positions in **DPE** in the presence of either N_2 or H_2 and between aromatic positions only when provoked by H_2 or D_2. Only a small amount of exchange between aromatic and aliphatic positions is observed under any conditions. The attack of D atoms at H-carrying aromatic positions makes H atoms available for transfer to other aromatic positions. The process results in a D_2-provoked generation of benzene-d_0. Mechanistic alternatives for these and other processes are discussed.

Introduction

A large volume of literature deals with the thermolysis of compounds which model the structure of coal.[1] Much less attention has been given to the reaction of coal models with molecular hydrogen although hydroliquefaction is a potentially important technology. An obvious approach to study of the H_2 reaction is to substitute D_2. The literature contains ample evidence that deuterium is incorporated into reaction products when thermolysis of coal and coal models is carried out under D_2 gas.[2] It has also been shown that D-labeled substrates, such as tetralin-d_{12}, transfer D atoms back to dihydrogen such that HD is produced from H_2.[3] Similarly it is clear that once incorporated into a molecule of organic substrate, transfer of D atoms between molecules is often facile under liquefaction conditions.[4] Several mechanisms can be involved in the exchange process. Molecule-induced homolysis and symmetry-allowed, pericyclic mechanisms have been documented by Brower and Pajak.[5] A demonstration of radical-promoted exchange was provided by King and Stock[6] who showed that the presence of species which undergo facile homolysis increases the rate of transfer of deuterium between benzylic positions in different molecules.

When exchange reactions are rapid, the question of how hydrogen is initially transferred from H_2 gas into the coal structure becomes especially difficult to answer because the initial landing site of the hydrogen atoms is rendered uncertain. Given the strength of the H−H bond, this initial step would seem likely to be a major obstacle to processes of interest and slower than subsequent events. A scheme put forward by Vernon[7] proposes hydrogen abstraction from H_2 by benzyl-type radicals. This suggestion, later supported by Shin,[8] 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 H_2. The phenomenon is less pronounced when the reactions are run in the presence of a hydrogen atom donor (tetralin or 9,10-dihydrophenanthrene). The reaction becomes prominent at high temperature.[9] However, benzene becomes an important product even in the absence of H_2 at high temperature.[10]

It is suggested that hydrogen atoms generated from the reaction of benzyl radicals with H_2 are responsible for the hydrogenolysis of the **DPE** to give benzene. In the presence of hydrogen−donor solvents, the benzyl radical accepts an H atom from the solvent to give toluene plus a more stable, presumably less reactive radical. The production of H atoms from the reaction with H_2 is thus reduced. The facility of reaction between benzyl radicals and compounds with structures similar to donor solvents is well documented.[11] 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 Price,[12] who showed that H atoms generated in the thermolysis of toluene above 500 °C react with toluene to produce CH_4 and H_2 with nearly equal rates.

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Also, it has been shown that the presence of H_2 promotes the conversion of tetralin to *n*-butylbenzene.[13]

The reaction between benzyl radicals and H_2 seems the most uncertain part of the scheme for hydrogen incorporation in that the C−H bond energy of toluene is 85 kcal/mol whereas that of H−H is 104 kcal/mol.[14] Nevertheless, Poutsma[1] has estimated that the disadvantage suffered by this reaction relative to the competing reaction between benzyl radical and unreacted diphenylethane is only a factor of 10 to 15, which is easily overcome if the pressure of H_2 is high, particularly for gas-phase reactions.

Despite the considerable literature discussed above, we felt that a thorough study of the reaction of model compounds with D_2 might be valuable. Assuming that some selectivity in the incorporation of D atoms is observed, it might be possible to do a more complete and possibly quantitative assessment of the various mechanistic steps involved. Accomplishing this might then allow prediction of how different structural units in coal would affect hydroliquefaction efficiency. At the very least it should be possible to show the limitations of this approach and to pinpoint the requirements for obtaining more detailed kinetic information.

Because most reported studies have utilized metal reactors, we were concerned that the walls of the reaction vessel or metal species contained in common reactor vessel sealants could be stopover points for D atoms prior to their introduction at the seminal sites for the exchange processes. If such 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.[15] As we wished to understand the noncatalyzed reaction and possibly to use it as a base line for further studies of catalytic agents, we designed and employed a glass reaction vessel for the studies reported below.

We chose **DPE** for our initial studies with D_2. Putting aside the question of how well it might represent the complex materials called coals, it is clearly the most thoroughly studied coal model compound[16] and we reasoned that the wealth of thermochemical information already available would help to direct our interpretations. We plan to use the information presented below to select new systems to expand the scope of our conclusions.

Experimental Section

Reaction Procedure. The reaction procedure, described in a preliminary publication,[17] places the reactants along with glass beads for agitation in a glass bulb of approximately 12 mL volume with a long capillary neck. 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 D_2 gas, closed off, and shaken at the desired temperature in a fluidized sand bath. Cold pressures were 800 psi of D_2 which translates to roughly 18 mmol of D_2 per mmol of **DPE** in a 300 mg (maximum **DPE** used) run. Runs with less **DPE** are specified in the tables. Temperatures listed in the tables are observed sand-bath temperatures which are possibly 10 to 15 degrees higher than actual temperatures inside of the reactor vessel based on thermocouple measurements. The latter were made with an unpressurized reaction vessel, however. Nevertheless, all runs were made with a similar apparatus under similar conditions and temperatures should, therefore, be comparable. Scatter in the data is no doubt due to uncertainties in day−to−day variations in the degree of correspondence between bath temperatures and internal temperatures of the reactor along with uncertainties in heat-up delays. However, the conclusions drawn in this paper do not rely on precision greater than current experimental reproducibility.

When the reaction is complete, carbon disulfide is added and products are removed for analysis using a long syringe needle. In the absence of gas generation within the tube, our observation has been that, at least for high concentration runs, an insignificant amount of 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. Product mixtures were analyzed by gas chromatography (GC) and by gas chromatography/mass spectrometry (GC/MS). Products present in substantial quantities were separated by preparative gas chromatography and analyzed by ^1H and ^2H NMR at 400 MHz in carbon disulfide. Calculation of deuterium distribution from mass spectral data was carried out with correction for P-1 peaks based on observed mass spectra of undeuterated compounds using the same equipment and conditions used for the analysis of reaction products. In all cases where major P-1 peaks were characteristic, it was assumed that H and D atoms were lost from the parent ion in proportion to their relative numbers in the particular isotopomer of interest. The appropriateness of this procedure was tested with compounds of known isotopic composition when they were available. Toluene, which at 70 eV gives the largest P-1 peak of all of the compounds studied (P-1/P = 1.6) was tested using commercially available toluene-d_3 and analyzed satisfactorily based on this approach. In studies subsequent to the present work, problems arose when very high deuterium levels were present in toluene, suggesting that our assumption of statistical loss of H and D breaks down. However, it seems to be satisfactory for the first few D atoms and would, at worst, affect mainly the D atom distribution and not the total amount of D. Data for stilbene are likely to be the least accurate because stilbene gives major P-1 and P-2 peaks and we had no standard stilbene of known D content to compare with. For other compounds analyzed, corrections for P-1 were relatively small. No attempt was made to analyze gaseous products.

Reactants. The syntheses of labeled **DPE** and of **TPB** have been described in preprints.[20,21]

Results and Discussion

Product Distribution under D_2. Preliminary details of the reaction of **DPE** with D_2 are described in an earlier communication.[17] A more complete description of the course of product formation is given in Table 1. Within experimental error, the data show the expected first-order loss of **DPE**.[17] Toluene (**1**) is the major product and represents a nearly constant fraction of the reaction products (55−63 mol %) up to 75% **DPE** conversion. The magnitude of this fraction is similar to values reported by Vernon.[7] It also agrees with data of Poutsma[18] and is in qualitative agreement with information provided by Miller and Stein[19] for reactions carried out

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Table 1. Product Distribution in the Thermolysis of DPE under D_2 at 450 °C

	time (min)								
	4	5	7	8	9	10	15	30	45
conversion (%)	8.8	10.7	18.8	21.1	23.4	29.4	39.1	63.4	75.0
product (mol %)									
$PhCH_3$ (**1**)	55.5	62.5	54.7	57.9	56.0	58.0	59.8	63.0	63.5
PhCH=CHPh (**2**)	7.8	6.1	9.5	5.4	8.5	6.2	5.3	1.7	0.6
$Ph_3C_3H_5$ (**3**)	6.3	7.2	6.7	5.5	6.1	4.4	3.1	1.0	0.4
PhH (**4**)	12.5	11.1	10.1	15.8	12.7	16.9	16.4	18.6	21.0
PhC_2H_5 (**5**)	10.8	6.5	11.1	9.7	9.8	10.3	10.0	11.3	10.7
Ph_2CHCH_3 (**6**)	2.1	2.1	2.4	2.0	2.1	1.9	2.1	1.9	1.7
Ph_2CH_2 (**7**)	0.2	0.1	0.2	0.1	0.2	0.2	0.4	0.5	0.5
$Ph_2C_3H_6$ (**8**)	0.1	0.1	0.2	0.9	0.5	0.7	0.6	0.6	0.5
$C_{14}H_{10}$ (**9**)	0.4		0.9		0.9	0.2	0.8	1.0	1.0
other	4.2	4.3	4.1	2.7	3.0	1.3	1.3	0.4	0.2

in the absence of an external hydrogen source. Stilbene (**2**) is produced but its relative amount varies somewhat unpredictably. As seen in Table 1, it was generally found to decrease at higher conversions, suggesting that it undergoes secondary reactions. We have found that the amount of **2** formed varies with the amount of **DPE** charged to the reaction tube. The runs used to construct Table 1 all employed approximately 300 mg of **DPE** in an approximately 12 mL reaction tube. If amounts less than 50 mg were used, **2** was found to represent a negligible fraction of the reaction products. 1,2,3-Triphenylpropane (**3**) is observed and also disappears at high conversion as might be expected.

As pointed out by Vernon for H_2,[7] the amounts of benzene (**4**) and ethylbenzene (**5**) are much higher when the reaction is carried out under D_2. In effect, the **2** formed in the absence of D_2 is replaced by these products. The amounts of **4** and **5** were found to be roughly equal in the initial stages of the reaction. At higher conversions, where analytical precision was improved, it seemed clear that the amount of **4** exceeded that of **5**, suggesting that **5** might undergo conversion to **4** under these conditions. The rearrangement product, 1,1-diphenylethane (**6**), remained a relatively constant fraction of the product mixture as conversion increased. Other products, formed in amounts too small for accurate determination, were diphenylmethane (**7**), 1,3–diphenylpropane (**8**), and phenanthrene (**9**). 1,2,3,4-Tetraphenylbutane (**TPB**) was present only in small amounts and is included in "other".

Deuterium Incorporation. The extent of deuteration in unreacted **DPE** as well as in significant products is reported in Table 2. Initial perusal of these data shows for some of the species a pattern suggestive of sequential exchange $d_0 \rightarrow d_1 \rightarrow d_2 \rightarrow$ etc. Calculated deuterium distributions for this scheme give a reasonable match of the GC/MS results for **DPE**, **1**, **2**, **3**, **7**, **8**, and **9**. It seems clear that the species above pick up D atoms at rates which are roughly proportional to the number of H atoms present despite the fact that both aromatic and aliphatic positions are involved. In fact, if a rate constant for approach to complete deuteration is calculated at each time for each of the compounds above, assuming that all H atoms in the molecule are available for exchange, a range of $k_{ex} = (6.5 \pm 1.5) \times 10^{-5}\ s^{-1}$ encompasses most data points. Figure 1 is a first-order plot for the loss of d_0 isotopomer of **DPE** and of several products. It will be seen that the plot for **DPE-d_0** extrapolates reasonably close to 100% **DPE-d_0** at the time origin and is steeper than the plots for single ring compounds, reflecting its greater number of reactive positions. The plot for **1-d_0** extrapolates near, but probably somewhat less than, 100% at the time origin, suggesting a small amount of direct reaction between benzyl radical and D_2. The plots for **5-d_0** and **6-d_0** clearly do not extrapolate to 100%.

Table 2. Deuterium Incorporation in 1,2-Diphenylethane and Products of Its Thermolysis Under D_2 at 450 °C

	time (min)					
product	5	8	10	15	30	45
DEP-d_0	76	66	56	41	14	8
DPE-d_1	21	28	33	38	29	21
DPE-d_2	3	6	9	16	29	28
DPE-d_3		1	2	5	17	23
DPE-d_4					7	13
DPE-d_5					2	5
1-d_0	80	78	74	64	45	37
1-d_1	18	20	22	29	36	36
1-d_2	2	2	4	6	14	19
1-d_3				1	4	6
2-d_0	77	70	65	58	36	29
2-d_1	18	23	27	30	33	31
2-d_2	5	6	7	4	20	22
2-d_3					8	12
2-d_4						5
3-d_0	64	51	42	29	7	2
3-d_1	30	35	37	36	19	10
3-d_2	6	11	16	23	26	19
3-d_3			5	9	23	24
3-d_4				3	15	21
3-d_5					8	14
3-d_6					3	7
4-d_0	48	54	38	40	46	40
4-d_1	49	39	48	44	41	41
4-d_2	3	7	14	15	12	16
4-d_3				1	2	3
5-d_0	48	42	38	33	18	13
5-d_1	45	45	44	43	34	29
5-d_2	7	12	16	19	29	30
5-d_3		1	3	5	14	18
5-d_4					4	7
6-d_0	49	40	34	21	9	6
6-d_1	42	43	42	38	24	18
6-d_2	9	15	19	27	30	27
6-d_3		33	3	10	22	24
6-d_4				3	11	15
6-d_5					4	7
7-d_0	79	67	61	51	30	23
7-d_1	21	27	30	34	33	29
7-d_2		6	9	12	22	24
7-d_3				3	10	14
7-d_4					4	6
8-d_0	74	53	43	29	6	1
8-d_1	26	38	39	39	22	11
8-d_2		9	18	24	32	22
8-d_3				8	25	26
8-d_4					12	22
8-d_5					3	13
9-d_0				49	25	18
9-d_1				35	34	29
9-d_2				13	25	27
9-d_3				3	12	16
9-d_4					4	7

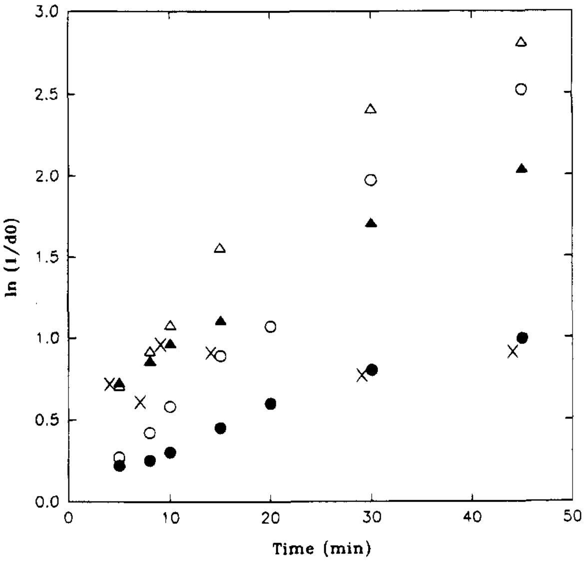

Figure 1. Plot of loss of d_0 isotopomer of **DPE** and selected products in the reaction of **DPE** with D_2 at 450 °C. Represented as ln (1/fraction of d_0 isotopomer) ○ = **DPE-d_0**, ● = **1-d_0**, ▲ = **5-d_0**, △ = **6-d_0** (X = **4-d_0** with points displaced 1 min closer to the time origin for visibility).

It is clear that the deuterium incorporation patterns for compounds **4**, **5**, and **6** are exceptional. For each of these cases, D content at the shortest reaction time is too high to be explained by the processes which exchange deuterium into **DPE** and products described above. For **4**, **5**, and **6**, it appears that approximately 50% of one atom of D is incorporated in the formation process. If this assumption is made and the exchange rate constants are calculated for additional D incorporation, they fall in the range of the rate constants for exchange of **DPE** and other products which were calculated without assuming initial D content.

To determine the location of D atoms in the molecules of interest, product mixtures were separated by gas chromatography and both ^1H and ^2H NMR spectra obtained when amounts of material allowed. The data are presented in Table 3. From the data for **DPE** itself, it is clear that hydrogen exchanges for deuterium at both aliphatic and aromatic positions. The ratio of aromatic D to aliphatic D has a remarkably constant value of (1.39 ± 0.03):1 for all time points. In **1**, the number of aromatic D atoms per molecule is approximately half that for **DPE**. This seems roughly what might be expected in that cleavage of **DPE** separates the aromatic rings. However, **1** must continue to exchange aromatic H atoms in order to keep pace with **DPE**, the result being maintenance of a roughly 2:1 ratio for D in **DPE** vs D in **1**. By contrast, the number of D atoms in the methyl group of **1** becomes somewhat less than half of the number in the two CH_2 groups in **DPE**, indicating that exchange in the CH_3 group is slower.

Table 3. Deuterium Location by NMR in Products from Thermolysis of DPE under D_2 at 450 °C

compd	time (min)	total D^a GC/MS	Ar−D^b NMR	D^b in −CH_2− by NMR	D^b in CH_3 by NMR
DPE	5	0.27	0.16 (0.10)	0.11 (0.07)	
	8	0.43	0.25 (0.13)	0.18 (0.09)	
	10	0.57	0.33 (0.30)	0.24 (0.22)	
	15	0.85	0.49 (0.45)	0.36 (0.33)	
	30	1.76	1.02 (0.91)	0.74 (0.65)	
	45	2.23	1.30 (1.04)	0.93 (0.75)	
1	8	0.24	0.12 (0.17)		0.12 (0.18)
	10	0.30	0.15 (0.21)		0.15 (0.20)
	15	0.41	0.22 (0.26)		0.19 (0.22)
	30	0.76	0.48 (0.65)		0.28 (0.39)
	45	0.92	0.57 (0.87)		0.35 (0.53)
5	15	0.96	0.32 (0.36)	0.16 (0.18)	0.48 (0.54)
	30	1.55	0.64 (0.50)	0.36 (0.28)	0.56 (0.44)
	45	1.81	0.93 (1.32)	0.38 (0.54)	0.50 (0.71)

[a] This is the number of D atoms per molecule calculated from data in Table 2. [b] D atoms in various positions were determined in two ways. The first data set uses the relative areas from ^2H NMR to determine the relative amounts of D in different environments but relies on MS data to determine the total D content. The second, values in parentheses, determines total D content using an internal NMR standard and does not rely on MS data. It is believed that the former should be more accurate.

D-Atom Generation. It is well established that thermolysis of **DPE** begins with cleavage of the central bond to give benzyl radicals, eq 1. In the presence of H_2 it has been proposed that the benzyl radicals react with H_2 to give **1** and H atoms as illustrated in eq 2. It is apparent from the relatively high amount of **1-d_0** at low conversions (Table 2) that this reaction is either not a major pathway to **1** or that **1** and **DPE** exchange aromatic H atoms very rapidly. In either case, it is necessary to conclude that the kinetically preferred process for benzyl radical is reaction with **DPE** as illustrated in eq 3 to give 1,2-diphenylethyl radical (**DPE**$^{\bullet}$). Once formed, **DPE**$^{\bullet}$ becomes available for reaction with D_2 by eq 4. Further complexity is contributed by the possibility for exchange reactions between **DPE** and **DPE**$^{\bullet}$, an example of which is shown in eq 5. To

$$\underset{\mathbf{DPE}}{\mathrm{PhCH_2CH_2Ph}} \longrightarrow 2\ \mathrm{PhCH_2^{\bullet}} \tag{1}$$

$$\mathrm{PhCH_2^{\bullet}} + \mathrm{D_2} \longrightarrow \underset{\mathbf{1\text{-}d_1}}{\mathrm{PhCH_2D}} + \mathrm{D^{\bullet}} \tag{2}$$

$$\mathrm{PhCH_2^{\bullet}} + \mathrm{DPE} \longrightarrow \underset{\mathbf{1\text{-}d_0}}{\mathrm{PhCH_3}} + \underset{\mathbf{DPE^{\bullet}}}{\mathrm{PhCH_2\dot{C}HPh}} \tag{3}$$

$$\mathrm{DPE^{\bullet}} + \mathrm{D_2} \longrightarrow \underset{\mathbf{DPE\text{-}d_1}}{\mathrm{PhCH_2CHDPh}} + \mathrm{D^{\bullet}} \tag{4}$$

$$\mathrm{DPE^{\bullet}} + \mathrm{DPE\text{-}d_1} \rightleftharpoons \mathrm{DPE} + \mathrm{DPE\text{-}d_1^{\bullet}} \tag{5}$$

estimate the relative importance of these processes, 1,2-diphenylethane-*1,1*-d_2 (**DPE-1,1-d_2**), was synthesized and thermolyzed under both N_2 and H_2. These results have been published earlier[20] and, in summary, showed that at 450 °C exchange of D atoms between **DPE** molecules is rapid, resulting in statistical distribution of **DPE-d_{0-4}** within 10 min. Under H_2, some D was lost, but this process is much slower, with a half-life of approximately 30 min. At 420 °C, exchange of **DPE** has a half-life of approximately 40 min and D distribution in **1** was strongly skewed to give **1-d_2** and **1-d_0**. The D distribution in **1** was slightly altered by changing from N_2 to H_2, but most of the change could be explained by changes in **DPE** prior to formation of **1**. Thus, the most straightforward explanation is that benzyl radicals react mainly with **DPE** and that the isotopic selectivity for this process is at least a factor of 3. Convincing confirmation of this

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[20] Rajagopal, V.; Guthrie, R. D.; Shi, B.; Davis, B. H. *Prepr. Pap.—Am. Chem. Soc. Div. Fuel Chem.* **1993**, *38*, 1114.

Table 4. Deuterium Content of Products of Reaction of Toluene-d_3 (40 mg), with 1,2-Diphenylethane-d_0 (25 mg) for 20 min at 450 °C under H_2

product	d_0	d_1	d_2	d_3	d_4
toluene	5.6	1.0	10.6	83.3	
DPE	58.0	33.5	7.6	0.9	0.04
benzene	98.8	1.2			
ethylbenzene	55.2	35.0	5.9		

Table 5. Product Distribution in the Reaction of 1,2,3,4-Tetraphenylbutane (TPB) under D_2 and N_2 at 400 °C[a]

	time (min)				
compd	5	10[b]	15	20[b]	30[b]
TPB	85	55 (66)	36	24 (51)	19 (34)
DPE	7	23 (12)	32	44 (18)	47 (31)
2	5	12 (12)	16	15 (18)	16 (26)
3	1.2	4.5 (8)	5	9 (12)	8 (8)
1	0.2	1.2 (0.7)	1.5	3 (0.7)	3.4 (0.9)

[a] These data are not identical to those in ref 21, due to improvements in analytical methods. [b] Numbers in parentheses refer to N_2 runs.

Table 6. Deuterium Content of Products from Thermolysis of TPB under D_2 at 400 °C

	time (min)				
% product	5	10	15	20	30
TPB-d_0	95	82	81	63	65
TPB-d_1	5	18	19	37	35
DPE-d_0	70	58	60	44	40
DPE-d_1	25	35	34	37	35
DPE-d_2	4	6	6	16	14
DPE-d_3		1	1	2	3
2-d_0	93	86	86	72	71
2-d_1	7	13	13	24	24
2-d_2		1	1	4	4
3-d_0		74	71	56	53
3-d_1		22	25	31	33
3-d_2		4	4	11	12
3-d_3				2	2
1-d_0		53	56	41	40
1-d_1		44	41	49	49
1-d_2		3	2	9	10

scheme was obtained by thermolysis of a mixture of 1,1,1-trideuteriotoluene with **DPE-d_0** under H_2. The details, given in Table 4, show that, after 20 min at 450 °C, D transfer from **1** to **DPE** has reached only 30% of that expected after complete equilibration. Thus it is clear that reactions of **DPE$^\bullet$** with **DPE** as shown in eq 5 are faster than reaction of **DPE$^\bullet$** with **1**, and while the latter reaction affects deuterium distribution at long reaction times, it does not alter the conclusion that the main reaction of benzyl radical is with **DPE** by eq 3.

1,2,3,4-Tetraphenylbutane (TPB). To provide additional evidence for the viability of **DPE$^\bullet$**-mediated D-atom generation, we studied the thermolysis of 1,2,3,4-tetraphenylbutane (**TPB**) under D_2. The results of this study have appeared in a preliminary communication,[21] but because of significant analytical improvements and additional data we present this information in Tables 5 and 6. It will be noted that under N_2, the reaction produces equal amounts of **2** and **DPE** as the major products. Clearly, **DPE$^\bullet$** formed from scission of the central bond in **TPB** (eq 6) in the absence of D_2 reacts with itself by disproportionation (eq 7). In the presence of D_2, there are no significant quantities of new products, but conversion of **TPB** is higher and the amounts of **DPE** become significantly greater than amounts of **2**. Because the temperature required for this reaction is below temperatures required for exchange of **DPE**, it seems unlikely that much redistribution of D takes place. Thus the observed incorporation of ca. 50% of one atom of D in initially formed **DPE** clearly shows that **DPE$^\bullet$** is capable of reaction with D_2 by eq 4 to give **DPE-d_1**. The increase in conversion probably indicates that the reaction of eq 6 is reversible and that roughly half of the **DPE$^\bullet$** radicals are trapped by D_2. Importantly, the D incorporation in **2** is significantly less than that in **DPE**, ruling out reaction of D_2 with **2** as a major route for D atom introduction. We have found that **2** will react with D_2 but higher temperatures are required. Studies of the noncatalytic reaction of alkenes with D_2 will be presented in a future publication.

$$2\ \mathrm{DPE}\cdot \rightleftharpoons \underset{\mathbf{TPB}}{\mathrm{PhCH_2CH(Ph)CH(Ph)CH_2Ph}} \qquad (6)$$

$$2\ \mathrm{DPE}\cdot \longrightarrow \underset{\mathbf{2}}{\mathrm{PhCH{=}CHPh}} + \mathrm{DPE} \qquad (7)$$

It will be noted that the small amount of **1** produced in the thermolysis of **TPB** contains only 53% of **1-d_0** at low conversions of **TPB**. In this case, benzyl radicals produced as minor fragmentation products clearly do react with D_2 by eq 2 probably because of lower concentrations of H atom donors. However, the larger fraction reacts with **DPE$^\bullet$** by coupling to give **3** and some may be involved in H atom removal from **DPE$^\bullet$**. Addition of benzyl radicals to **2** is another possible route to **3**; however the similar amounts of **DPE** and **2** in the N_2 runs are difficult to explain if this is an important path.

Mass spectral analysis of recovered **TPB** is inherently inaccurate due to facile fragmentation of its parent ion. However, an approximate analysis based on apparent D content of its weak parent ion and of the base peak at 181 amu suggests that incorporation in recovered **TPB** is relatively low. This may be due to the relatively low volatility of **TPB** limiting access by D atoms. The D incorporation in recovered **TPB** is similar to that in **2**, suggesting that a certain fraction of **DPE$^\bullet$** is produced as a secondary reaction of **2** (eq 14) and that this radical can either give **2** by eq 7 or return to **TPB** by the reverse of eq 6.

Study of D-Labeled Compounds. Returning to the reaction of **DPE** with D_2 it remains to discuss the mechanism for deuterium substitution in aromatic rings. Data in Table 3 show that all products from the reaction of **DPE** with D_2 exhibit similar extent of aromatic H replacement by D. In the reactions of **DPE-1,1-d_2** under N_2, it was found[20] that there was very little transfer of aliphatic D atoms to aromatic positions. A small amount of this process was observed in the N_2 runs but it disappeared under H_2. It seems clear that aromatic exchange is a result of the production of D atoms by reaction of **DPE$^\bullet$** with D_2 (eq 4) followed by the sequence of eqs 8 and 9. In view of the similar rates of D incorporation (per phenyl ring) for all compounds present, it seems clear that the reaction of eq 8 does not discriminate significantly among the available substrates.

Because the reaction of H atoms with D_2, eq 10, is known to be a fast process,[22] it might be wondered why the sequence of eqs 8, 9, and 10 does not provide a kinetic chain for the rapid exchange of all aromatic hydrogens. Results in Table 3 show a slight excess of aromatic over

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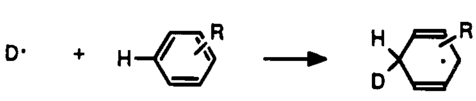
[21] Ramakrishnan, S.; Guthrie, R. D.; Shi, B.; Davis, B. H. *Prepr. Pap.-Am. Chem. Soc. Div. Fuel Chem.* **1993**, *38*, 1122.



(8)

(9)

$$H^{\cdot} + D_2 \longrightarrow HD + D^{\cdot} \qquad (10)$$

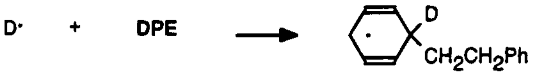
aliphatic D, but nothing which would suggest a chain reaction of substantial length. To explain the shortness of chains, we considered the possibility that the adduct radical formed in eq 8 might be involved in chain-terminating disproportionation reactions with benzylic radicals. To test this possibility, we synthesized and studied 1,2-di(phenyl-d_5)ethane (**DPE-d_{10}**). Results for thermolysis under N_2 and under H_2 are presented in Table 7. Examination of the ^2H NMR of recovered **DPE** showed that D transfer to aliphatic positions is less than 0.1 atom of D per molecule under N_2 and about 0.15 atom of D per molecule under H_2 for the 20 min runs at 450 °C. Thus the presence of H_2 provokes a small amount of D atom transfer to aliphatic positions, but this is unlikely to represent an important termination process. It seems more likely that aliphatic deuteration arises from D atoms released by the reverse of eq 9 followed by the reverse of eq 8. These D atoms can react with **2**, leading back to deuterated **DPE**. As expected, the presence of H_2 produces extensive replacement of D by H. Interestingly, when equimolar amounts of **DPE-d_0** and **DPE-d_{10}** were thermolyzed under H_2, transfer of H and D atoms between aromatic sites in different molecules was observed (column 5, Table 7). This is particularly evident in the amount of **DPE-d_1** produced, ca. 27% of the initial **DPE-d_0**. Calculations suggest that this is unlikely to be explained by the amount of HD present in the H_2. Also the amount of exchange in the **DPE-d_{10}** has measurably increased. Two explanations seem possible. One is that the intermediate H or D atom adduct transfers H or D from one molecule to another as suggested by McMillen and Malhotra.[23] Another is that D atoms generated in the reaction of H atoms with **DPE-d_{10}** react with **DPE-d_0** faster than they react with H_2. A rate constant for the addition of H atoms to aromatic rings does not seem to be available, but the rate constant for addition to ethene is approximately 6.3×10^9 M^{-1} s^{-1} at 450 °C.[24] As this is ca. 100 times greater than the rate constant for eq 10[22] and the concentration of H_2 is about 100 times that of **DPE** in the experiments of Table 7, it seems necessary to also consider the possibility that **DPE** and H_2 compete for D atoms. Both explanations seem viable on the basis of available data.

Details of Aromatic Substitution. There is some scatter in the benzene (**4**) yield data presented in Table 1, but for the first six points, the average mole fraction of **4** in the products is about 12.5%. This is comparable to the amount of **5** at low conversions, in agreement with Vernon's[7] suggestion that **4** and **5** are produced by eqs 11 and 12. Although it is possible that a small amount of the **4** and **5** produced could be due to an elimination reaction of **DPE**$^{\cdot}$ to give styrene and phenyl radical, such a scheme could not, by itself, explain the increased yields of **4** and **5** observed when H_2 or D_2 runs are compared with N_2 runs.

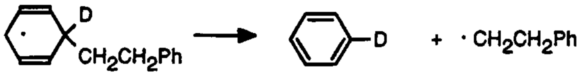
Table 7. Thermolysis of 1,2-Di(phenyl-d_5)ethane (DPE-d_{10}) at 450 °C

	reaction under N_2			reaction under H_2	
d_n	0 min	20 min	30 min	20 min	20 min[a]
d_{10}	59	55	51	2	<1
d_9	24	22	22	8.5	1.4
d_8	7	8	9	17	3.5
d_7	2.6	3.2	4.0	22	7.5
d_6	1.7	2.6	3.7	20	8.7
d_5	1.6	2.2	2.9	13	9.1
d_4	2.0	2.6	3.2	7.0	6.6
d_3	1.3	1.5	1.7	3.6	5.8
d_2	<1	<1	<1	2.4	3.8
d_1	<1	<1	<1	1.8	13.5
d_0	<1	<1	<1	1.5	39.3

[a] For this experiment, equal amounts of **DPE**-d_{10} and **DPE**-d_0 material were mixed such that the total number of moles of diphenylethane was the same as present in the other experiments.



(11)



4-d_1

(12)

Comparing the yield of **4** (Tables 1 and 2) with the extent of aromatic deuteration in **DPE** (Table 3) for the first three data points in Table 2 gives a ratio of (average D atoms in **DPE**)/benzene yield = 11 ± 3. At least initially, 50% of the benzene is undeuterated, presumably reflecting roughly equal attack of H and D atoms on **DPE**. This being the case, attack by D atoms on **DPE** leads to deuterium incorporation in **DPE** 22 ± 6 times as often as it leads to **4-d_1**. After correction for the statistical advantage for five non-*ipso* positions, we arrive at an apparent kinetic factor of roughly 4 favoring attack at unsubstituted positions. However, the calculation considers only attachments which are successful in producing deuterated product. For the simple benzene derivatives present in these reaction mixtures, it seems likely that significant fraction (up to one-half) of attachments do not produce deuteration *i.e.*, eq 8 is reversible whereas eq 11 very likely is not. This then suggests that the factor of 4 represents a lower-limit kinetic preference for the unsubstituted positions.

More Reactive Radicals. The 2-phenylethyl radical produced in the reaction of eq 12 can abstract D from D_2 or H from available aliphatic C−H groups. It might be guessed that the radicals leading to **5** and **6**, 2-phenylethyl radical and 2,2-diphenylethyl radicals, respectively, being less stable due to lack of the resonance stabilization available to benzyl and **DPE**$^{\cdot}$ radicals, react with hydrogen donors in a relatively indiscriminate fashion. This would explain the relatively high initial D content of both **5** and **6** in Table 2 and the fact that plots for **5-d_0** and **6-d_0** do not extrapolate to 100% values in Figure 1. This interpretation is supported by data in Table 3 showing that **5** contains significantly more D in its CH_3 group than

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[22] Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976; p 148. Information taken from Baldwin, R. R.; Melvin, A. J. *J. Chem. Soc.* **1964**, 1785. Log $k = 10.7 - 9.4/\phi$ which at 450 °C corresponds to $k = 4.7 \times 10^7$ M^{-1} s^{-1}.

[23] (a) Malhortra, R.; McMillen, D. F. *Energy Fuels* **1993**, *7*, 227–223. (b) McMillen, D. F.; Malhotra, R.; Chang, S.-J.; Ogier, W. C.; Nigenda, S. E.; Fleming, R. H. *Fuel* **1987**, *66*, 1611–1620. (c) Malhotra, R.; McMillen, D. F. *Energy Fuels* **1990**, *4*, 184. (d) McMillen, D. F.; Malhotra, R.; Nigenda, S. E. *Fuel* **1989**, *68*, 380. (e) McMillen. D. F.; Malhotra, R.; Hum, G. P.; Chang, S.-J. *Energy Fuels* **1987**, *1*, 193.

[24] See ref 22, p 168.

its CH_2 group. The greater reactivity fortuitously results in reaction with D_2 to give D atom incorporation in about half of the events leading to **5** and **6**, the balance being reactions with H atom donors such as **DPE** itself.

Additional Considerations. Equations 1 and 3–13 and other reactions discussed above explain the major products and their deuterium incorporation patterns. However, if eq 2 is not important then eq 14 must be added in order to accommodate the stoichiometry of the main transformation (**DPE** + $H_2 \rightarrow 2$ **1**). This stoichiometry can be obtained by summing eqs 1, 3, 4, 7, and 14 (with appropriate coefficients and replacing D by H). If H and D atoms can add to benzene rings, they can surely add to **2** so it is clear that eq 14 should be a viable process. Equation 14 also explains the gradual loss of **2** with increasing conversion (Table 1). The sequence of eqs 14 and 4 provide a mechanism for the noncatalytic hydrogenation of alkenes. We have found that **2** will react slowly with D_2 at 450 °C and that the rate of this process is increased by the presence of **DPE**.

$$D_2 \text{ or DPE} + {}^{\bullet}CH_2CH_2Ph \longrightarrow \underset{\mathbf{5}\text{ or }\mathbf{5}\text{-}d_1}{H(D)CH_2CH_2Ph} \quad (13)$$

$$H^{\bullet}(D^{\bullet}) + \underset{\mathbf{2}}{PhCH{=}CHPh} \longrightarrow DPE^{\bullet} \text{ or } DPE\text{-}d_1^{\bullet} \quad (14)$$

Effect of DPE Concentration. Manka and Stein[25] have shown that, for solution reactions at 150 °C, a wide variety of benzylic radicals, including **DPE**$^{\bullet}$ undergo coupling faster than disproportionation. However, under the conditions of our study, coupling processes leading to **TPB** and **3** are reversible. Therefore, the only evident termination reaction for the listed sequences is the disproportionation of **DPE**$^{\bullet}$, eq 7. It seems clear that it is this reaction which limits the efficiency of deuterium incorporation in **DPE** and presumably also the associated "hydrocracking" reaction to give **4** and **5**. It is predictable that kinetic chains would be lengthened if the disproportionation reaction could be slowed. In future publications we will explore substrate structural changes which accomplish this. However, a simple approach is to lower the concentration of **DPE** in the reaction vessel. While this will reduce the rate of all bimolecular reactions, the reaction between two **DPE**$^{\bullet}$ radicals should be more affected than the reaction between **DPE**$^{\bullet}$ and D_2. Experimental confirmation of this prediction is presented in Table 8. Run A was carried out with approximately the same amount of material used for runs described in Tables 1–3 and, for the most part, is in good agreement.[26] Runs B and C successively decreased the amount of **DPE** charged to the ca. 12 mL reaction vessel. It is clear from Table 8 that the D content of all species increases dramatically. The amount of $\mathbf{d_0}$ material drops under 10% for most species and the extent of multiple deuteration increases. Table 8 shows that for this 6-fold decrease in **DPE** concentration, the D content increase is a factor of ca. 4 in the aromatic positions and ca. 2 in aliphatic positions. Although the kinetic situation is very complex, it is apparent that the chain length of the sequence of eqs 8, 9, and 10 has become greater. It would therefore be expected that the relative yield of **4** and **5** should also increase, and although it was more difficult to avoid loss of **4** for low concentration runs, the ratio of **1** to **5** drops from a factor of 5 to 6 at high **DPE** to less than 2 at low **DPE**. Thus the length of the eq 11, eq 12, eq 13 chain is also increased.

Table 8. Deuterium Location by NMR as a Function of DPE Concentration and D_2 Pressure at 450 °C for 20 Min

compd	run[a]	total D[b] GC/MS	Ar–D[c] NMR	D[c] in $-CH_2-$ by NMR	D[c] in CH_3 by NMR
DPE	A	1.00	0.58	0.42	
	B	1.58	0.99	0.59	
	C	3.25	2.47	0.78	
	D	3.20	2.39	0.81	
	E	1.42	0.96	0.46	
1	A	0.54	0.33		0.21
	B	0.98	0.65		0.33
	C	2.13	1.59		0.54
	D	0.76	1.84		0.62
	E	0.92	0.99		0.39
5	A	1.04	0.34	0.22	0.48
	B	1.55	0.67	0.23	0.65
	C	2.61	1.30	0.37	0.93
	D	2.35	1.33	0.27	0.75
	E	1.48	0.77	<0.30	0.71

[a] Run codes: A = 300 mg of **DPE**, 800 psi D_2 (cold). B = 150 mg of **DPE**, 800 psi D_2. *C* = 50 mg of **DPE**, 800 psi D_2. D = 50 mg of **DPE**, 600 psi D_2. E = 50 mg of **DPE**, 400 psi D_2. [b] This is the number of D atoms per molecule calculated from mass spectral data. [c] D atoms in various positions were determined using ^2H NMR to determine the relative amounts of D in different environments and MS data to determine the total D content.

Summary and Relevance to Coal Hydroliquefaction

This study provides a mechanistic model for the hydroliquefaction of coal in the absence of metal catalysts. Heating produces radicals through thermolysis of relatively weak bonds. Hydrogen transfer between component species builds the concentration of more stable radicals which can either react with H_2 or undergo termination. As termination by disproportionation is less reversible than coupling, this seems likely to be the main barrier to increasing kinetic chain lengths, as it is in our model. Hydrogen atoms produced through the reaction of these radicals with H_2 react reversibly at unsubstituted ring positions but also displace alkyl substituents as reactive radicals which propagate short kinetic chains through reaction with H_2. For the model compound studied, H atom adducts to aromatic rings are shown not to be involved in termination processes. However, this will almost certainly be different for coal where H atom adducts of polycyclic aromatic compounds are expected to be more stable and are more likely to function kinetically in the manner of the 1,2-diphenylethyl radicals in this study. The scheme suggests that the presence of H atom donors such as tetralin and dihydrophenanthrene may show limited benefits to hydroliquefaction efficiency in that the radicals produced by H atom transfer can readily disproportionate. If radicals can be prevented from reacting with each other, efficiencies should increase. Lowering substrate concentration, while a simple expedient in the model system, is not so easy for coal. The reduced mobility of radicals in coal should be an advantage, but possibly limited access by H_2 could counteract this. Study of surface-immobilized models is planned.

Acknowledgment. The authors thank the United States Department of Energy, Pittsburgh, for a grant, DE-FG22-91-PC91291, supporting this work.

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[25] Manka, M. J.; Stein, S. E. *J. Phys. Chem.* **1984**, *88*, 5914–5919.

[26] Benzene shows a greater amount of d_0 content in run A than in either the 15 or 30 min run in Table 2. It is believed that this may be due to improvements in separation of benzene from solvent which became available for run A.