

THERMOLYSIS OF SILICA-IMMOBILIZED 1-(4'-HYDROXYPHENYL)-2-PHENYLETHANE UNDER D₂: A HYDROLIQUEFACTION MODEL.

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INTRODUCTION

In previous work, reactions of coal model compounds with D₂ at temperatures to 450 °C and pressures of 2000 psi in isolation from metal surfaces were studied. The distribution of deuterium in recovered starting materials and products, determined by GC/MS and by ¹H and ²H NMR allowed identification of viable pathways for hydroliquefaction with increased certainty. Studies carried out with 1,2-diphenylethane (bibenzyl), DPE,¹ various deuterium-labeled diphenylethanes,² 1,2,3,4-tetraphenylbutane,³ 2,2,5,5-tetramethyl-3,4-diphenylhexane,⁴ and 1-[4-(2-phenylethyl)benzyl]naphthalene⁵ model a mechanistic scheme for hydroliquefaction in which radicals formed by the homolysis of weak bonds, react with D₂ in competition with hydrogen-atom abstraction from benzylic sites. The reaction with D₂ produces deuterium atoms which react reversibly at unsubstituted positions in monocyclic aromatic compounds by the sequence of eqs 1 and 2.



where H-Ar represents any aromatic compound. Eq 2 is probably a two-step process. Reaction of D or H atoms at alkyl-substituted positions produces alkyl radicals as proposed by Vernon.⁶ These react relatively unselectively with available H- and D-atom donors. Kinetic chains involving D (H) atoms are short because of addition of these species to alkenes and polycyclic arenes as well as abstraction of benzylic C-H. The radicals produced in these processes undergo termination through disproportionation, reducing overall hydrocracking efficiency.

In 1986, Buchanan, Poutsma and coworkers demonstrated that the attachment of 1-(4'-hydroxyphenyl)-2-phenylethane, DPE-OH, to a silica surface via a carbon-oxygen-silicon linkage dramatically changes the distribution of thermolysis products when compared with unattached DPE in the absence of H₂.⁷ Large increases in the amounts of rearrangement and cyclization products, removed from the surface subsequent to thermolysis, signaled the involvement of radicals which were not free to undergo the chain transfer and termination processes typical of solution and gas-phase chemistry. Subsequently, Buchanan, Britt and Biggs, for several different substrates, showed that H-atom transfer reactions on silica surfaces can be moderated by the presence of labile H-atoms in interspersed spacer molecules.⁸

We felt it would be interesting and instructive, concerning possible effects produced by the restricted mobility of the coal matrix, to examine the reaction of surface-immobilized substrates under hydroliquefaction conditions with D₂. Clearly, in order for the results to be easily interpretable, the substrates must not be removed from the surface through the action of D₂. Earlier temperature-programmed hydrolysis experiments suggested that this would not be a problem.⁹

EXPERIMENTAL

DPE-OH was attached to fumed silica (Cabosil M-5, Cabot Corp.) in the manner prescribed by

Buchanan, et. al.⁷ The sample used for the experiments reported in Tables I and II had a surface loading of 0.32 or 0.51 mmoles/g. Samples of surface-attached material (500 mg) were placed in glass reactors described earlier.¹ The substrate was heated under N₂ or D₂ pressure in a fluidized sand bath. Temperatures reported are corrected by using a thermocouple-containing reactor and are measured under H₂. Times reported are actual time-in-bath measurements and should be shortened by approximately 5 min to allow for a measured 8 min heat-up period. Reaction mixtures were analyzed by vacuum transfer of volatile materials at 2 X 10⁻³ Torr and 80 - 100 °C into a liquid nitrogen-cooled trap for 2 h. The contents of the trap were treated with a measured amount of biphenyl in CH₂Cl₂ and the solution analyzed by gas chromatography on a 30 m, 0.25 mm capillary column coated with DB-1 at 0.25 μm. Samples were also subjected to GC/MS analysis. After removal of volatile materials, the residual coated silica (150 - 200 mg samples) was hydrolyzed with 30 to 35 mL of 1 N NaOH for 12 to 16 h at 25 °C then treated with a measured amount of a standard solution of 4-hydroxybiphenyl in 0.1 N NaOH. The hydrolysis mixture was acidified and extracted with CH₂Cl₂. After removal of the solvent, the residue was treated with a solution of N,O-bis(trimethylsilyl)trifluoroacetamide containing pyridine and trimethylsilyl chloride. The trimethylsilylated material was analyzed by GC and GC/MS as described above. Control experiments to document silica-promoted aromatic hydrogen exchange were carried out by sealing phenol-d₆ (Aldrich Chemical Co.) with Cabosil and any other desired reactants into a ca. 7" X 10 mm Pyrex tube under argon and heating for the desired time. Work up was carried out as described above for N₂ and D₂ reactions.

RESULTS AND DISCUSSION

Hydropyrolysis of DPE-OH attached to fumed silica at a coverage of 0.51 mmoles/g (close to maximum level) at 410 °C was carried out under both N₂ and D₂ at 2000 psi in a glass reactor as previously described for the hydropyrolysis of DPE.¹ The reactor design is necessarily different from that employed by Buchanan, Britt, and coworkers^{7,8,9} in their studies of silica-bound DPE-OH which was configured so that volatile products, including small amounts of phenol driven from the surface in the early stages of the reaction were continuously removed from the reaction zone. In the present study, volatile materials remain in the hot reactor throughout the heating period. The product distribution under N₂ pressure (Table I) is, nevertheless, consistent with that previously reported in vacuum with a relatively high yield of rearrangement product, HOPhCHMePh (isolated after hydrolysis of silica as its trimethylsilylated derivative).⁷ For comparison purposes, we have carried out the gas-phase thermolysis of DPE-OH itself in D₂ under comparable conditions and found the amount of HOPhCHMePh to be less than 0.5 mole%. Thus, D₂ does not diminish the rearrangement reaction under conditions of restricted mass transport.

The most significant effect of D₂ is the increased yields of hydrocracking products: benzene, ethylbenzene (PhEt), phenol (PhOH) and 4-ethylphenol (EtPhOH) shown in Table I. Also, the amount of 4'-hydroxystilbene (HOPhCH=CHPh), is reduced under D₂. These effects were also observed in the hydropyrolysis of free DPE.^{1,6}

An unanticipated outcome of the surface attachment experiments was the change in deuterium distribution pattern. Table II summarizes the free DPE-OH data (column 3) and compares them to those for silica-attached DPE-OH, DPE-OSi, (columns 1 and 2). In comparing 10 min runs for attached and free material it is apparent that the preference for deuterium incorporation in oxygen-substituted rings has increased substantially for DPE-OSi. This is particularly evident in the material with lower surface coverage, column 1, where the D content of oxygen-substituted rings is two to three times greater than that of unsubstituted rings. This effect is particularly dramatic (a factor of 3 to 6) where the different rings of DPE-OH are compared, but is also evident when comparing PhMe with HOPhMe, etc. This selectivity is somewhat reduced for high coverage DPE-OSi at 410 °C but is observed for this material as well at lower temperature.¹⁰

In previous experiments with DPE, it was clear that in the presence of thermolysis-produced radicals, aromatic exchange takes place by eqs 1 and 2. It is reasonable to assume that the same sequence occurs for DPE-OH. Because radical reactions might be expected to be insensitive to ring substituents, particularly at the temperatures involved, it was expected, and indeed found, that when DPE-OH is heated with D₂ the unsubstituted and HO-substituted rings contain equal numbers of D atoms after reaction.

We suspected that the most reasonable explanation for selective deuteration of oxygen-substituted rings is that the exchange process becomes electrophilic. If, for example, the underivatized SiOH groups remaining on the surface were somehow to be converted to SiOD groups it seemed possible that, at temperatures of the order of 400 °C, these might catalyze exchange at suitably

reactive ring positions. To test this, we subjected phenol- d_6 to treatment with silica (Cabosil) at 400 °C and indeed observed exchange. With excess silica, up to three of the ring D atoms in phenol- d_6 could be replaced by H. Moreover, a mixture of phenol- d_6 and MePhOH heated with silica produced MePhOH deuterated at ring positions. The temperature threshold for the exchange of phenol- d_6 with silica could be shown to be about 140 °C and thus at 400 °C, the exchange goes rapidly to an equilibrium distribution. Thus it seemed clear that, were a mechanism available to exchange D atoms from D_2 with SiOH groups on the silica, our results could be explained. In support of this scheme, we were able to determine the presence of SiOD groups on recovered silica by infrared spectroscopy after removal of volatile products. It is important to note that the silica-catalyzed exchange reaction (using phenol- d_6), in the absence of D_2 , works only for phenolic compounds and not for benzene or even for anisole (methyl phenyl ether).

It seems almost certain, despite the apparently heterolytic nature of the reaction of SiOD with PhOH, the exchange of SiOH with D_2 , moderated by phenolic compounds, must have radical components. D_2 thermolysis of surface-attached PhOH, Ph-OSi, which offers no obvious route for radical production, led to some exchange in the recovered PhOH. However, the amount of D is small relative to comparable DPE-OSi experiments and, moreover, radical processes must contribute even here as evidenced by the formation of trace amounts of benzene with relatively high D content.

We have noted above that small amounts of phenolic compounds driven from the surface and removed from the reaction zone in vacuum experiments^{7,8,9} remain in the reaction vessel under the conditions of the present studies. The phenolic species are presumably generated by a process analogous to that for dehydroxylation of silica at elevated temperatures ($\equiv\text{Si-OAr} + \equiv\text{Si-OH} \rightarrow \equiv\text{Si-O-Si} \equiv + \text{HOAr}$). Moreover, molecules of water adsorbed on the surface prior to reaction are available to hydrolyze Si-OAr bonds under D_2 . Under present conditions, this typically leads to 5 to 10% of free phenolic material (based on materials obtained following vacuum transfer).

Stein,¹¹ Bockrath,¹² and others have noted that even though the ArO-H and ArCH₂-H bond energies are about the same, H abstraction by ArO• radicals is inherently faster. At 170 °C, Bockrath¹² has found that benzyl radicals abstract H atoms from ArO-H roughly 15 times faster than from benzylic structures in PhCH₂CH₂Ph, etc. Given that radicals produced in these thermolyses seem likely to be reacting with small amounts of phenolic compounds shown to be free of the surface (eq 3), the phenoxy radicals produced seem certain to react with D_2 to produce D atoms by eq 4.



D atoms produced in this way could be involved in the usual exchange at aromatic sites (eq 2), but could also react with phenols by eq 5.



The reactions of eqs 4 and 5 constitute a chain process which results in the conversion of HOAr to DOAr. This would presumably also occur in the thermolysis of DPE-OH under D_2 and, therefore, of itself, must not be sufficient to produce selective exchange in O-substituted rings. However, if, in the presence of silica, exchange of O-substituted rings with DOAr is catalyzed, selective D incorporation can be explained. To document the viability of eq 3, we heated DPE with phenol- $O-d$ and showed deuterium to be present in the toluene produced.

Focussing on the non-oxygen-substituted rings reveals evidence that the free radical chain for H/D substitution is more efficient for gas-phase species than for surface immobilized molecules. Cleavage-produced free molecules, benzene, PhMe, PhEt as well as DPE (presumably formed by radical recombination) contain at least twice as much deuterium as the unoxxygenated ring in recovered DPE-OH suggesting that the latter is a less active participant in the D-atom promoted exchange.¹³ Particularly convincing is the lower D content of PhCH₂ fragments from DPE-OH as compared with those from PhEt. As DPE-OH spends most of its time on the surface, this argues that D atoms react predominantly with gas-phase substrates.

SUMMARY

The important conclusions of this study are: 1. The presence of D_2 at 2000 psi does not alter the

tendency of surface-attached radicals to rearrange. 2. Hydrocracking is observed for hydropyrolysis of surface-attached materials. 3. Radical D/H exchange is more efficient in the gas phase. 4. The reaction of benzylic radicals with phenols has been documented. 5. Phenoxy radicals catalyze exchange between D₂ and SiOH groups on silica which in turn promotes exchange at ortho and para ring positions in phenolic compounds.

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13. It may be noticed that the D content of benzene, toluene and ethylbenzene from free DPE-OH is also high, but this is misleading because the DPE-OH reaction proceeded to higher conversion.

Table I. Product Distribution in the Thermolysis of Surface-Attached 4'-Hydroxy-1,2-diphenylethane at 410 °C under N₂ and D₂. Coverage = 0.51 Mmoles/g.

Mole % of Total Products

Product ^a	10 min/N ₂	10 min/D ₂	30 min/N ₂	30 min/D ₂
Benzene	1.2	6.0	0.5	6.9
PhMe	28.6	25.9	31.5	22.8
PhEt	0.8	5.5	1.0	7.0
PhCH ₂ CH ₂ Ph	0.7	2.6	1.0	1.9
PhCH=CHPh	----	---	0.3	<0.02
TMSOPh ^b	2.8	6.8	1.3	8.7
TMSOPhMe ^b	27.4	23.3	28.6	27.5
TMSOPhEt ^b	0.8	4.8	1.2	6.2
TMSOPhCH ₂ Ph ^c	1.5	1.1	3.7	1.9
TMSOPhCHMePh ^c	11.3	11.5	9.2	11.3
TMSOPhenH ₂ ^{c,d}	<0.3	---	0.3	----
TMSOPhCH=CHPh ^c	23.2	10.7	18.6	2.6
TMSOPhen ^{c,d}	1.8	1.7	2.8	3.2

^a Conversions were 33.5, 26.8, 53.0 and 58.1% for the 4 runs. Recoveries of listed products ranged from 75 to 85%. A few GC peaks for which tentative identification can be made are not listed. Majority appear to be siloxytriphenylpropane isomers. Some styrene may be present. A large number of very small unidentified peaks were observed for which individual peaks represent less than 0.05 mole %.

^b Represents sum of volatile and hydrolysis-recovered products. ^c These were measured after hydrolysis of recovered silica and trimethylsilylation. ^d Phen = phenanthryl, PhenH₂ = dihydrophenanthryl.

Table II. Deuterium Content of Products from Thermolysis of DPE-OSi and DPE-OH for 10 Minutes at 410 °C Under D₂.

Average Number of D Atoms per Molecule

Product	DPE-OSi (0.32) ^a	DPE-OSi (0.51) ^a	DPE-OH ^c
Benzene	1.11	1.01	0.87
PhMe	0.66	0.95	0.80
PhEt	1.19	1.29	1.10
--> PhCH ₂ ^d	0.74	0.69	0.43
PhOH	2.50 (2.55) ^b	1.55 (1.22) ^b	0.95 (0.91) ^b
MePhOH	2.20 (2.01) ^b	1.43 (1.09) ^b	0.79 (0.77) ^b
EtPhOH	2.37 (2.34) ^b	1.69 (1.23) ^b	1.23 (1.30) ^b
^d --> PhCH ₂ ^d	1.99	1.25	0.50
PhCH ₂ CH ₂ Ph	3.25	1.77	1.07
^d --> PhCH ₂ ^d	1.87	0.90	0.59
TMSOPhCHMePh	2.23	0.90	1.12
TMSOPhCH ₂ CH ₂ Ph	2.1	1.04	0.82
^d --> PhCH ₂ ^d	0.34	0.24	0.46
^d --> TMSOPhCH ₂ ^d	1.9	0.89	0.47

^a Surface coverage in mmoles/g. ^b First value is for vacuum-transferred material. () represents trimethylsilylation products after hydrolysis of silica. The difference at high coverage appears to be real. Hydrolysis procedures do not change D content. ^c Conversion was higher for this material (60%) compared to 22% and 27% for first two columns. ^d Mass spectral fragment.