

SURFACE CHARACTERIZATION OF
IRON OXIDE DISPERSED ON SUBBITUMINOUS COAL.

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ABSTRACT

The preparation and characterization of Wyodak subbituminous coal impregnated with 0.1-1.0 wt% iron by the incipient wetness technique have been studied. X-ray photoelectron spectroscopy (XPS) was used to examine the surface chemistry versus the bulk composition of the iron oxide loaded on the coal particles. The effects of Fe concentration, $\text{NH}_4\text{OH}/\text{Fe}$ ratios and coal drying on the speciation of Fe are reported. The relative concentration of FeOOH and Fe_2O_3 on the surface is a function of coal drying. The direct liquefaction performance of the different Fe loaded coal samples is related to the specific Fe concentrations.

INTRODUCTION

Small particle iron oxide catalyst precursor deposited on coal by an incipient wetness (IW) technique provided improved conversion and distillate yields in direct liquefaction.¹ In this technique coal is impregnated with a metal salt solution which when added to the coal reaches the point where unbound moisture begins to form drops.² In the case of iron salts, addition of base produces finely divided iron oxyhydroxide. SEM analysis showed that iron impregnated by IW using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was primarily deposited on the surface of the coal.³ Subsequently, coal is dried to remove the excess moisture before subjecting it to liquefaction. Sulfidation that occurs during liquefaction presumably does not result in any significant growth of the iron particles upon conversion to pyrrhotite,⁴ although recent results indicate that pretreatment at lower temperatures provide increased liquefaction performance because of more efficient conversion of the precursor oxide to pyrrhotite.⁵ Distillate yields from liquefaction of 5000 ppm Fe-impregnated Wyodak coal were greater than from the corresponding liquefaction when using pigment grade iron oxide plus added sulfur.⁶

Impregnating coals by IW is a multi-step process involving first the distribution of the metal solution onto the coal, after which the oxide is formed, presumably at the point of contact with the base material. Since preparation proceeds through a series of steps involving coal preparation, metals impregnation, base precipitation, filtration, washing, and drying, all which may alter the subsequent liquefaction performance of the impregnated coal.

This paper describes the results of a study to evaluate the performance of an Fe-impregnated Wyodak coal. The effects of several independent variables in the preparation scheme on metal dispersion and chemical form were investigated using XPS. This technique has been used not only to analyze the surface composition of coals⁷ but also to characterize the surface composition, elemental distribution and chemical state of the Fe-O system, including Fe_2O_3 , Fe_3O_4 , FeO , and FeOOH .⁸ In addition, the conversion and product distribution from liquefaction of several of

these Fe-impregnated coals are discussed.

EXPERIMENTAL

Impregnated Coals - Wyodak coal from the Black Thunder Mine in Wright, Wyoming, which was provided by CONSOL, Inc., was ground to -200 mesh, riffled and stored under nitrogen at 4°C. Proximate and ultimate analyses of the coal are presented in Table 1. IW-coal samples were prepared starting with either as-received coal or coal predried at 110°C/10 Torr/20 hrs. The moisture content and the volume of water used in the IW-impregnation of as-received coal were 21 wt% and 0.75 ml/g dry coal, respectively, and for impregnation of predried coal were 2-3 wt% and 0.90 ml/g dry coal, respectively. Solutions containing $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, purchased from Aldrich Chemical Co., were slowly added in a dropwise manner to the coal while mixing to assure even distribution. 1.5M NH_4OH was added to these samples at a $\text{NH}_4\text{OH}/\text{Fe}$ mole ratio from 31 to 138. The aqueous slurries were filtered and the samples were dried at 40°C/20 hrs/10 Torr, unless otherwise specified. Water washing, if performed, preceded the drying step.

XPS Measurements - The XPS of the various samples of Fe impregnated coal was carried out with the LHS-10 Leybold-Heraeus Spectroscope using Mg K α radiation with 15 Kv, 20 mA and pass energy of 100 ev. The powdered samples were mounted on the XPS sample probe with Double-Stick Scotch tape. The sample powders were gently pressed and covered all of the Scotch tape attached on the stainless steel foil. The analysis chamber vacuum was about 5×10^{-9} Torr. The C_{1s} , O_{1s} , Fe_{2p} , Fe_{3p} , N_{1s} , Ca_{2p} , Al_{2p} , Si_{2p} , and S_{2p} elemental spectra and the survey spectra of the coal samples were obtained under the above working conditions and corrected with the hydrocarbon C_{1s} binding energy 284.6 ev. The elemental concentrations were calculated and the peak deconvoluted with a computer aided program of damped non-linear least squares curve fitting, using mixed Gaussian/Lorentzian profiles.⁹

Equipment and Procedures - Liquefaction experiments were performed in 50 ml microautoclaves to which were added 3 grams of coal, 5.4 grams of tetralin, and 1.2 mol dimethyl disulfide/mole added Fe. The reactors were sealed, pressurized with hydrogen to 1000 psig, and leak tested. Reactions were carried out in a fluidized sandbath set at the specified temperature while the reactors were continuously agitated at a rate of 400 cycles per minute. Reactors were then quenched to ambient temperature, the gaseous products collected and analyzed, and the products separated into THF insoluble (IOM), THF soluble-pentane insoluble (PA+A), and pentane soluble (oils+water) fractions. The product distribution was calculated assuming complete recovery of ash and conversion of catalyst to pyrrhotite ($\text{Fe}_{0.9}\text{S}$). The total of the net products equals the amount of maf coal in the feed and reflects the net make of each of the solubility fractions; coal conversion equals 100 minus the yield of IOM.

RESULTS AND DISCUSSION

The volume of water used in the IW-impregnation of as-received coal containing 21 wt% moisture was 0.75 ml/g, which was 20% less than for dry coal (0.90 ml/g). Ferric nitrate has sufficient solubility that this difference in the volume of water was not limiting. The incorporation of the metal onto the coal was essentially quantitative as determined by analysis of filtrates collected during preparation. The analysis of filtrates from addition of 1.5M NH_4OH , which causes precipitation of Fe as FeOOH , and filtrates from subsequent water

washes, indicated negligible Ca exchange and Fe bypass (see Table 2). In the NH_4OH treatment, only 0.1 wt% of the Ca originally in the coal was removed with about the same amount recovered in a subsequent water wash. Less than 0.01 wt% of the Fe added to the coal was found in both filtrates. The extent of NH_4^+ exchange corresponding with formation of ammonium carboxylates is presumably quite small. NO_3^- recoveries in the NH_4OH filtrates ranged from 83 wt% up to 119 wt% and were accurate only to $\pm 20\%$. The absence of NO_3^- ions in the washwater filtrate indicates substantially complete removal in the NH_4OH filtrate which makes water washing unnecessary.

Fe Distribution - Surface and bulk concentrations determined for metals (Fe, Ca, Al, Si), C, O, N and S for both impregnated as-received and predried coals are presented in Table 3. The surface of the dry as-received Black Thunder coal without any added Fe is enriched in the concentration of Fe, O, Al and Si, which reflects particle fracturing along the mineral surfaces during grinding. In the impregnated samples, the Fe concentration on the surface was significantly higher than in the bulk and increased with the amount of added Fe. In those samples that were final dried at $40^\circ\text{C}/10$ Torr/20 hrs, the concentration on the surface reached 6.3 wt% (CH-41) at the 1.0 wt% Fe addition level versus 12.5 wt% (CH-45) in the sample dried in flowing nitrogen at $40^\circ\text{C}/20$ hrs, the maximum observed in this study. This difference in surface Fe concentration suggests significant penetration of the iron within the cracks, crevices and pores of the coal particles. For each of these samples the relative concentration of oxygen on the surface increased as the iron concentration increased. Carbon fluctuated between samples and sulfur was generally lower at the surface relative to the bulk.

The increased surface Fe concentration of two impregnated predried samples suggests that diffusion of the Fe salt into these coals was hindered. Thermal pretreatment apparently results in sufficient transformation within the coal structure to block diffusion of the Fe-containing aqueous phase into the particle. Maintaining the integrity of the aqueous phase within the particle, as in the as-received samples, promotes diffusion of the Fe ions into the particle.

Surface Chemistry - Fe-IW impregnated coals show XPS spectra with Fe_{2p} peaks appearing at 711.2 eV ($\text{Fe}_{2p\ 3/2}$) and 725.1 eV ($\text{Fe}_{2p\ 1/2}$), Fe_{3p} at 56.6 eV and O_{1s} at 531.3 eV. The known spectra of FeOOH provides a good fit with the observed spectra. For those coals having low Fe loadings the O_{1s} peak is shifted to a higher binding energy of 532.4 (CH-20, CH-11) which approaches that of the O_{1s} binding energy in the spectra of the starting coal. This higher binding energy is consistent with greater participation of the O_{1s} peaks for Al_2O_3 and SiO_2 , which are located at 531.8 and 532.8 eV, respectively. The binding energy of the N_{1s} peak was found to be 399.5 eV which is consistent with organic nitrogen in the coal which precludes the presence of any significant amount of NH^+ or NO_3^- . Interpretation of the form of the added Fe is not complicated by the iron in the original coal since the $\text{Fe}_{2p\ 3/2}$ peak at 709.3 eV and a Fe_{3p} peak at 52.3 eV are considerably lower than observed. These lower binding energies are consistent with Fe-O and Fe-S structures. For the samples dried at about 110°C (CH-2), the decrease in the Fe_{3p} binding energy to 56.0 eV indicates the appearance of Fe_2O_3 , that occurs as the FeOOH particles on the surface agglomerate. Likewise, deconvolution of the O_{1s} envelope indicates a lower binding energy peak at 530.0 eV consistent with the presence of the Fe_2O_3 species. In general, the Fe_{2p} spectra are broadened and highly complex due to multiplet splitting

effects which are characteristic of oxides. The samples developed significant electrical charge during analysis consistent with the low electrical conductivity of Fe oxyhydroxide.

Liquefaction of Impregnated Coals - No significant effect on THF conversion or product distribution was observed as a result of varying the NH_4OH treatment over a range of NH_4^+/Fe ratios from 31 to 138. Likewise, subjecting the coals to a final wash also had no effect on liquefaction. Fe, however, had a definite effect on both oil yield and THF conversion as shown in Table 4. A sharp increase in both THF conversion and oil yield occurred with addition of 2800 ppm Fe; conversion increased from 81 wt% to 86 wt% while oils+water increased from 38 wt% to 44 wt%. Further addition of Fe up to 1.0 wt% resulted in smaller increases in both conversion and oil+water yields.

CONCLUSIONS

XPS spectra show a high degree of Fe dispersion on the coal surface with significant diffusion of Fe into the cracks, crevices and pore structure of the coal. The surface Fe concentration was higher on coals predried at 110°C before adding the Fe salt, indicating reduced metal diffusion into the coal. XPS supports Fe being present both as FeOOH and Fe_2O_3 . Addition of 2800 ppm Fe causes a sizable increase in both THF conversion and oils+water yield. Increasing the Fe concentration up to 1 wt% causes still further increases in both conversion and oil+water yield, though to a lesser extent.

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Table 1. Proximate, Ultimate and Ash Analysis of Black Thunder Wyodak Coal

	As Received ^a	Dry ^b
Proximate, as-received basis		
Moisture	22.4	2.63
Ash	5.46	5.66
Volatile Matter	34.4 ^c	45.47
Fixed Carbon	39.8 ^c	46.2
Ultimate, Dry		
Carbon	70.32	72.15
Hydrogen	4.68	4.34
Nitrogen	1.04	1.23
Sulfur	0.50	0.53
Chlorine	0.035	-
Oxygen	16.74	15.93
Ash	6.69	5.81
Ash Composition, wt%		
Fe ₂ O ₃	5.48	-
CaO	21.34	-
Al ₂ O ₃	15.76	-
SiO ₂	31.48	-
MgO	4.3	-
Na ₂ O	0.48	-
K ₂ O	0.49	-
TiO ₂	1.14	-
P ₂ O ₅	0.96	-
SO ₃	17.26	-

^a Analysis provided by Consol, Inc. ^b Dried 110°C/20 hrs/10 Torr. ^c Determined at UK/CAER.

Table 2. Filtrate Analysis^a

Coal Sample No.	NH ₄ OH Filtrate		Washwater Filtrate	
	CH-3	CH-21	CH-4 ^b	CH-22 ^c
Fe ⁺³ Added, wt% dry coal	1.0	0.55	1.0	0.55
Ca, wt% dry coal	1.0	1.0	-	-
Calcium Recovery, wt% Ca in dry coal	0.10	0.11	0.12	0.02
Fe Recovery, wt% Added Fe ($\times 10^2$)	0.1	3.0	9.8	3.1
NO ₃ ⁻ Recovery, wt% ^d	83	93	^e	^e

^a Direct Current Plasma Emission Spectrometry (DCP). ^b CH-4 originated from CH-3.

^c CH-22 originated from CH-21. ^d Measured using ion specific electrode; values $\pm 18\%$.

^e NO₃⁻ was not detected in these solutions.

Table 3. Surface Concentration of Elements as Determined by XPS^{a,b}

As Received	Starting Coal ^c	Moisture wt%	Added Fe	Fe	C	O ^d	N	Ca	Al	Si	S
	-	22.4		(0.19)	(57.8)	(29.6)	(1.2)	(0.75)	(0.56)	(1.1)	(0.46)
CH-BT	AR	2.6	0	0.33	71.1 (70.3)	20.6 (17.8)	1.3 (1.2)	0.5	2.0	4.0	0.2 (0.5)
CH-10	AR	3.6	0.15	1.0	62.3	25.5	1.4	1.0	3.4	3.5	n.a. ^e
CH-11	AR	1.8	0.28	1.4	66.2	23.5	1.7	1.0	2.4	3.5	0.3
CH-13 ^f	AR	5.4	0.28	1.9	64.1	23.9	1.7	1.2	3.1	3.8	0.3
CH-1	PD	1.4	0.28	2.7	63.5 (67.4)	24.7 (19.4)	1.7 (1.5)	1.0	2.5	3.6	0.4 (0.4)
CH-20	AR	0	0.55	2.4	63.5	25.2	1.5	1.0	2.9	3.3	0.2
CH-8 ^g	AR	5.4	0.77	3.2	66.8 (68.1)	20.2 (19.2)	0.8 (1.8)	0.7	1.9	4.6	n.a. (0.4)
CH-31	AR	2.9	0.77	4.2	62.4	24.8	1.2	1.0	2.5	3.3	0.6
CH-41	AR	2.7	1.0	6.3	59.6	25.6	1.6	1.0	3.8	3.4	0.3
CH-3	PD	3.9	1.0	8.3	54.2 (65.4)	28.2 (21.2)	1.0 (1.6)	0.8	3.8	3.1	0.4 (0.5)
CH-45 ^f	AR	6.1	1.0	12.5	49.3	30.7	0.8	0.3	3.8	2.5	0.1

a. () Bulk composition, wt% of sample.

b. Starting coal impregnated with Fe(NO₃)₃·9H₂O in 0.74 ml water/g for as-received coal and 0.90 ml/g for predried coal, treated with 1.54M NH₄OH at 138 NH₄⁺/Fe ratio, vacuum filtered, and dried at 40°C/10 Torr/20 hrs.

c. AR is as-received coal, PD is predried coal at 110°C/10 Torr/20 hrs.

d. Includes oxygen associated with moisture in sample.

e. n.a., not available

f. Dried at 40°C/1 atm/flowing N₂/20 hrs.

g. Washed with 1.54M NH₄OH at 31 NH₄⁺/Fe ratio.

Table 4. Product Distribution from Liquefaction of Fe IW-Impregnated Coals

Sample No.		CH-11	CH-20	CH-8	CH-41	CH-45
Fe Added, wt% dry coal	0 ^a	0.28	0.55	0.77	1.0	1.0
S/Fe ^b	0	2.9	1.0	1.3	1.2	1.3
Moisture, wt%	1.8	2.5	0	3.4	2.7	6.1
Product, wt% maf coal						
HC Gases	1.0	1.1	1.1	1.1	1.2	1.2
CO ₂ +CO	4.0	3.7	3.6	4.1	3.9	3.8
Oils + Water	38.3	44.1	44.9	45.1	46.4	48.0
PA + A	37.9	37.5	37.0	38.7	37.9	36.1
IOM	18.8	13.6	13.4	11.0	10.6	10.9
THF Conv	81.2	86.4	86.6	89.0	89.4	89.1
mg H ₂ /g maf coal	26	38	40	36	40	45

a. Coal dried 90°C/125 Torr/20 hrs.

b. Mole ratio of added S in DMDS to added Fe.

REACTION OF DEUTERIUM-LABELED 1,2-DIPHENYLETHANE WITH H₂

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INTRODUCTION

In a previous report, we described experiments carried out in a glass reactor in which 1,2-diphenylethane, DPE, was observed to react with D₂ at 450 °C to give extensive deuterium incorporation in both starting DPE and reaction products.¹ Examination of compounds present by ¹H and ²H NMR showed the presence of deuterium in both aliphatic and aromatic positions with somewhat more aromatic D than aliphatic D. Toluene and recovered DPE contained similar amounts of D, 10 - 20% of one atom of D per molecule at low conversions of DPE but increasing with increasing conversion. Certain products, benzene, ethylbenzene, and 1,1-diphenylethane, contained initially higher amounts of deuterium, 50% of one atom or greater, signalling distinct mechanistic pathways.

It was thus suggested that benzyl radicals formed through homolysis of the 1,2-bond in DPE react mainly with unconverted DPE to give toluene and 1,2-diphenylethyl radicals, accounting for the fact that 80% of the initially formed toluene contained no deuterium. The 1,2-diphenylethyl radicals produced were implicated in the removal of D atoms from D₂. Recently we have shown that 1,2-diphenylethyl radicals generated by an alternate path at lower temperatures are, indeed, capable of promoting reaction with D₂.² Our earlier work also supported the suggestion of Vernon³ that H atoms produced through the reaction of radicals with H₂ are responsible for the hydrocracking of DPE to give benzene and 2-phenylethyl radicals in that the reaction under D₂ gave ethylbenzene with a relatively high D content in the methyl group and D-enriched benzene.

Because the literature contains abundant evidence that exchange of hydrogens is facile between benzylic positions,⁴ we undertook to determine the extent to which transfer of deuterium between various positions in DPE might complicate our mechanistic conclusions. To this end we have carried out experiments with DPE-1,1-d₂ (two aliphatic hydrogens replaced) and DPE-d₁₀ (aromatic hydrogens replaced). The results force modification of our earlier scheme and lead to important new insights.

RESULTS AND DISCUSSION

1,2-Diphenylethane-1,1-d₂, DPE-d₂. This compound was prepared as described in the Experimental Section. Tables I and II present data obtained by GC/MS on recovered diphenylethane and product toluene from the thermolysis of DPE-d₂ at 450 °C under N₂ and under H₂. As will be

noted, at short time periods, listed at < 5 min, 96 to 98% of all diphenylethane molecules contain two atoms of D. This is essentially identical to the composition of starting material. The two D atoms in this material and in the starting material are shown to be positioned on the same atom by the mass spectral fragmentation pattern which shows fragments at m/z of 91 and 93 with very little spectral intensity at $m/z = 92$. After 10 or 15 min at 450 °C, redistribution is evident both under H_2 and under N_2 . It is also apparent that the distribution of D atoms does not change significantly with additional heating (30 min). This indicates that equilibrium is reached after roughly 10 min at 450 °C. Significantly, none of the mass spectra show molecular ions containing more than four atoms of D as would be the case if exchange included the aromatic positions.

One experiment was also carried out with a mixture of toluene-1,1,1- d_3 and DPE- d_0 for 20 min at 450 °C under H_2 . Deuterium transfer to DPE was observed, but this was not extensive, indicating that toluene is a less active partner in the exchange process than is DPE. This is expected based on the relative stabilities of benzyl radicals and 1,2-diphenylethyl radicals.

The non involvement of the aromatic hydrogens was confirmed by NMR measurements combining 1H and 2H NMR in the manner described in our earlier report. These data, shown in Table III, show a small amount of D transfer to the aromatic ring positions under N_2 . Aromatic D in the H_2 experiments is too small to detect. NMR experiments on toluene produced showed no significant aromatic D, however, detection limits for toluene were higher because of small sample size. NMR determination of aliphatic D in toluene gave results in agreement with those obtained by MS.

Importantly, it was also observed that the benzene produced in the H_2 runs contained no significant amount of D by MS measurement. The benzene produced in the N_2 runs, albeit formed in very small amount, showed about 25% of one atom of D per molecule. This suggests that a mechanism exists for the expulsion of D atoms from the benzylic positions but that they react with the aromatic ring only in the absence of H_2 . This clearly indicates that the reaction $D \cdot + H_2 \rightarrow H \cdot + HD$ is rapid under the reaction conditions.

Comparison of the runs carried out under H_2 shows that there is a gradual removal of D from DPE molecules such that approximately half of the original D content of the starting DPE is lost after 30 min at 450 °C. This process is partly due to the reaction of benzyl or 1,2-diphenylethyl radicals with H_2 to add H atoms to the mixture of starting materials and products. This dilutes the aliphatic D present in diphenylethane after its hydrogens are mixed with other aliphatic hydrogens, presumably including those of toluene. However, this is not the entire story because there appears to be a net loss of D from the system and this can also be explained by the expulsion of D atoms from the 1,2 diphenylethylradical as discussed above.

The reaction described above was carried out at a lower temperature to allow observation of the exchange process with greater precision. The results are presented in Tables IV and V. In Table IV it is clear that the exchange of D atoms between DPE molecules is proceeding, but even after 40 min is some distance from the equilibrium situation reached in Table I. It will be noted that in recovered DPE, d_1 molecules accumulate more rapidly than d_3 molecules despite the fact that at equilibrium (Table I - N_2) they become equal. As the formation of DPE- d_1 involves removal of D and replacement with H

whereas DPE-d₃ requires removal of H and replacement by D, the observed distribution suggests a larger isotopic preference in the replacement process. It is not obvious why this should be so, but the situation is complicated because isotope effects on two reactions are involved.

The deuterium content of the toluene produced from DPE-1,1-d₂ at 420 °C, presented in Table V, is particularly interesting. The total of d₀ plus d₁ toluene molecules is nearly equal to that of d₂ plus d₃, indicating that roughly half of the toluene arises from d₁ benzyl radicals and half from d₀ benzyl radicals. It is also clear that each of these radicals pick up H atoms in preference to D atoms. At least in the experiment carried out under N₂, the only source of hydrogen would appear to be the DPE molecules themselves. Thus it would appear that there is a average isotope effect for the removal of H from DPE by benzyl radicals of roughly $k_H/k_D = 4.6$. It is curious that benzyl-d₂ radicals and benzyl-d₀ appear to be showing somewhat different isotope effects, but this could be an artifact of the analysis of the mass spectral data which is complicated in the case of toluene by facile fragmentation. Also, at longer times, significant scrambling within the DPE occurs prior to conversion to toluene. Nevertheless, the observed isotope effect is almost certainly real and is consistent with studies by Bockrath who found values of 6.5 to 8.0 for the reaction of benzyl radical with a variety hydrogen atom donors at 170 °C in solution.⁵ Comparing the H₂ and N₂ data for toluene shows that there is slightly more D in the toluene from the N₂ runs, but it is not clear whether this comes from H₂ or whether it simply reflects the loss of D from DPE. We are attempting to analyze this situation in greater detail. It seems clear that the major source of H atoms in the toluene formed is the DPE molecule and, at most, about 10 % comes from H₂.

1,2-Di(phenyl-d₆)ethane. This compound was prepared by reaction of 2-phenylethyl chloride with benzene-d₆ and AlCl₃. As it turned out, aromatic exchange with reaction-generated DCl is quite facile giving 1,2-diphenylethane with more than 5 D atoms. By treating the product with more benzene-d₆, AlCl₃ and a trace of D₂O we were able to obtain material which was largely d₁₀. NMR experiments showed no D in aliphatic positions. Preliminary data for the thermolysis of the d₁₀ compound at 450 °C is shown in Table VI. The composition of the diphenylethane recovered after thermolysis under N₂ is essentially that of the synthesized material. The data thus strongly suggest that there is very little transfer of hydrogen from aliphatic to aromatic positions. We presume there is a small amount, based on the experiments with d₂ material, but the present experiment is too insensitive to measure it. Because there is no significant amount of d₁₁ material, it seems probable that there is little or no transfer of D from aromatic to aliphatic positions. This is confirmed by ²H NMR which shows that the amount of aliphatic D is undetectably small in the N₂ experiment (<0.1 atom of D per molecule) and barely measurable in the H₂ experiment (0.15 atom of D per molecule).

These results are particularly important in that they rule out termination steps involving aromatic H-atom adducts. In our previous analysis of the overall process for the thermolysis of diphenylethane under D₂,¹ we suggested a scheme in which H- or D-atom adducts transferred H or D atoms to the various benzylic radicals in termination steps. The experiments with d₁₀ material rule out any significant contribution from such processes. This leaves us without termination steps for the sequence. As it is clear that long chains are not involved (D incorporation does not greatly exceed the amount of conversion to products in D₂ reactions) we need to invoke a

different termination process. The evidence of facile disproportionation of 1,2-diphenylethyl radicals shown in the tetraphenylbutane experiments,² suggests that this is the most important termination step in the DPE reactions.

SUMMARY AND CONCLUSIONS

What is now known about the reaction of diphenylethane with hydrogen?

The first and second steps in Figure 1 are well precedented and general accepted. They are also supported by our work in that we have shown that the dominant reaction of benzyl radicals is with unreacted DPE. The generation of H atoms by the reaction of benzylic radicals with H₂ also is accepted and our work suggests that the 1,2-diphenylethyl radical may be the dominant participant in this process as shown in the fourth reaction in Figure 1.

What now happens to the H atom? Clearly it adds to aromatic rings as evidenced by the incorporation of D when D₂ is used. However, the adducts must be too unstable to survive at concentrations high enough to react with either benzyl or diphenylethyl radicals as shown by the experiments with d₁₀ material. Thus when an H atom reacts with an aromatic ring, it simply generates another H atom (or occasionally a 2-phenylethyl radical but this most likely reacts with H₂ to give another H atom). Because the reverse of the fourth reaction is an energetically downhill reaction, it seems likely that most H atoms will simply give back 1,2-diphenylethyl radicals by H-atom extraction from DPE. If, however, stilbene is present, another option presents itself, that of the fifth reaction in Figure 1 which also gives a diphenylethyl radical. With disproportionation of 1,2-diphenylethyl radicals included as shown in the third equation in Figure 1, the third and fifth steps constitute a route for disposal of H atoms. Combining the five processes in Figure 1, in proper proportion totals to a stoichiometrically correct result for the conversion of diphenylethane to toluene.

The mechanism would then work as follows. Benzyl radicals are formed and equilibrate with 1,2-diphenylethyl radicals. This process is clearly demonstrated by scrambling, etc. 1,2-diphenylethyl radicals having no exothermic reaction available other than reversible dimerization to a species which is unstable at 450 °C (tetraphenylbutane) or disproportionation, build to relatively high concentrations and disproportionate. When the occasional H atom is formed, it adds reversibly to aromatic rings, extracts H atoms from benzylic positions and reacts with stilbene formed in the disproportionation. At low substrate concentrations, the reaction of radicals with H₂, present at high concentration is favored and relatively little stilbene accumulates.

If this sequence is correct, it would explain the relatively high amounts of deuterium incorporated in DPE which is formed as a side reaction in the thermolysis of 2,2,5,5-tetramethyl-3,4-diphenylhexane.⁶ We have found that stilbene is formed as a side reaction in thermolysis of this compound. If it is serving as a D-atom scavenger, this would explain not only why DPE enriched in D₂ is found, but also why there is relatively little aromatic D incorporation in other products. Considering that we now know that D-atom adducts of phenyl rings do not build up in these systems, it is reasonable to presume that the reaction of D atoms with phenyl rings is somewhat endothermic. This being the case, stilbene may be an effective scavenger of wandering H

(or D) atoms. We are presently trying to design experiments to demonstrate the role of stilbene.

There are a number of potentially important implications of this analysis. It would, for example, suggest that a role of catalyst in promoting cleavage of Ar-R bonds in coal liquefaction and related model studies could be simply to facilitate hydrogenation of species which might otherwise trap H atoms. In coal, the role of H-atom trap would likely be played by various polynuclear aromatic compounds as well as various reaction-produced elimination products. A paper by Bockrath, Schroeder and Keldsen reports an effect of 9-methylanthracene which could be interpreted in this way.⁷ A thorough understanding of this phenomenon might lead to a better design for catalysts. We are excited about the relative simplicity and the potential implications of this model.

EXPERIMENTAL

2-Phenylethanol-1,1-d₂. Methyl phenylacetate (3.5 g, 23.2 mmol) was dissolved in ether to make a ca. 1 M solution and this was added to a 1 M ether solution containing 1 g of LiAlD₄ at 25 °C. This was allowed to stir under N₂ for 30 min. This was treated with a saturated solution of NH₄Cl in water and the ether layer separated. The ether layer was dried with anh Na₂SO₄ and the solvent removed by rotary evaporation. ¹H NMR (CDCl₃) δ 2.85 (s, 2.0 H), 7.2 (m, 5 H). This was used without further purification.

2-Phenylethyl chloride-1,1-d₂. The alcohol prepared above (2.0 g, 16 mmol) was treated with 10 mL SOCl₂ and 4 mL pyridine and the reaction mixture was stirred at 25 °C for 30 min followed by cautious treatment with about 10 mL water. The resultant mixture was extracted with 50 mL ether. The ether was dried and evaporated as above. This was used without purification in the following reaction.

1,2-Diphenylethane-1,1-d₂. The crude chloride prepared above (1.4 g, 9.9 mmol) was dissolved in 10 mL of spectrometric grade benzene and this was added to anhydrous aluminum chloride (1.5 g, 11.3 mmol) at 0 °C. The reaction mixture was stirred for 40 min followed by treatment with water and extraction with ether (ca. 75 mL of each). Drying and removal of ether as before gave crude product. This was purified by column chromatography on silica gel in hexane to give 1.02 g of product mp 48-50 °C, ¹H NMR (CDCl₃) δ 2.91 (s, 2.0 H), 7.2 (m, 10 H). MS gave m/z 184, 93, 91.

1,2-Di(phenyl-d₅)ethane. 2-Phenylethyl chloride (2.0 g, 14.2 mmol) was dissolved in benzene-d₆ (5 g, 58 mmol) and the solution added to aluminum chloride (2.8 g, 22.6 mmol) following the procedure described above. The crude product was redissolved in fresh benzene-d₆ and treated with fresh AlCl₃ and a drop of D₂O. Work-up and purification as described above gave product mp 48-50 °C. ¹H NMR (CDCl₃) δ 2.92 (s), aromatic resonance was less than 5% of the aliphatic resonance. MS gave m/z 192, 96.

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Table I. Composition of 1,2-Diphenylethane after Thermolysis of 1,2-Diphenylethans-1,1-d₂ at 450 °C.

	d ₀	d ₁	d ₂	d ₃	d ₄
<5 min (H ₂)	1.75	1.49	96.4	0.12	0.15
10 min (H ₂)	26.3	29.8	32.3	11.3	0.4
30 min (H ₂)	29.7	41.7	22.5	5.5	0.6
<5 min (N ₂)	1.6	0.7	97.5	0.1	0.1
15 min (N ₂)	5.6	22.9	46.3	21.7	3.0
30 min (N ₂)	7.8	23.8	42.2	22.4	3.8

Table II. Toluene from Thermolysis of Diphenylethane-1,1-d₂ at 450 °C.

	d ₀	d ₁	d ₂	d ₃
<5 min (H ₂)	44.3	4.8	50.1	0.8
10 min (H ₂)	34.0	32.5	30.1	3.4
30 min (H ₂)	42.1	43.3	13.1	1.5
<5 min (N ₂)	---	---	---	---
15 min (N ₂)	26.2	30.1	35.9	7.8
30 min (N ₂)	25.4	31.9	35.3	7.5

Table III. NMR Analysis of Recovered Diphenylethane from Thermolysis of 1,2-Diphenylethane-1,1-d₂.

Conditions	D atoms/molecule	
	aliphatic	aromatic
H ₂ (10 min)	1.96	<0.09
H ₂ (30 min)	1.19	<0.09
N ₂ (15 min)	1.98	0.09
N ₂ (30 min)	1.84	0.16

Table IV. Composition of 1,2-Diphenylethane after Thermolysis of 1,2-Diphenylethane-1,1-d₂ at 420 °C.

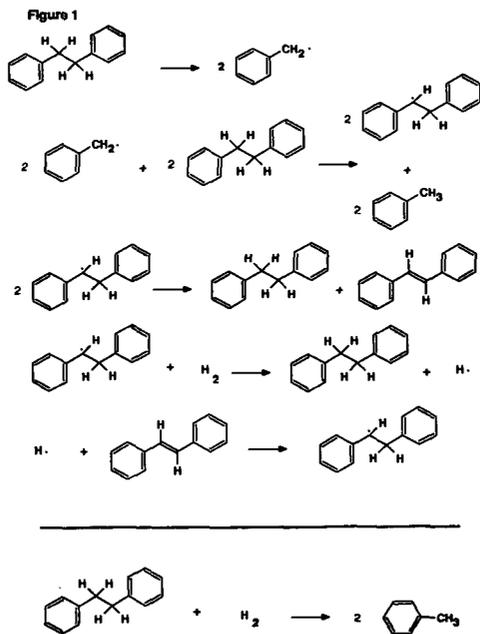
	d ₀	d ₁	d ₂	d ₃	d ₄
10 min (H ₂)	0.4	12.0	86.0	1.5	0.17
20 min (H ₂)	2.3	19.6	73.6	4.2	0.18
40 min (H ₂)	5.9	29.5	59.5	5.0	0.20
10 min (N ₂)	1.6	4.8	91.6	2.0	0.1
20 min (N ₂)	1.6	11.1	83.1	4.0	0.1
40 min (N ₂)	2.9	16.5	71.6	8.7	0.3

Table V. Toluene from Thermolysis of Diphenylethane-1,1-d₂ at 420 °C.

	d ₀	d ₁	d ₂	d ₃
10 min (H ₂)	42.8	7.6	46.7	3.0
20 min (H ₂)	40.3	12.4	42.8	4.5
40 min (H ₂)	41.2	16.3	39.4	3.0
10 min (N ₂)	37.3	10.9	45.0	6.7
20 min (N ₂)	37.1	13.2	41.9	7.8
40 min (N ₂)	33.5	17.1	39.6	9.8

Table VI. Thermolysis of 1,2-Di(phenyl- d_3)ethane (DPE) at 450° C (20 min).

Composition	Reaction under N_2		Reaction under H_2	
	DPE %	Toluene %	DPE %	Toluene %
d_{10}	55	--	2	--
d_9	22	--	8.5	--
d_8	8	--	17.4	--
d_7	3.2	--	22.3	--
d_6	2.6	--	20.2	--
d_5	2.2	59	13.2	11.4
d_4	--	32	7.0	31.8
d_3	--	9	3.6	33.8
d_2	--	--	2.4	13.8
d_1	--	--	1.8	6.8
d_0	--	--	1.5	2.4



REACTION OF 1,2,3,4-TETRAPHENYLBUTANE WITH D₂ AT 400 °C

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INTRODUCTION

In an earlier preprint,¹ we have described the reaction of diphenylethane, DPE, with D₂ at 450 °C to promote D incorporation in both starting DPE and reaction products. A previous study by Vernon² had suggested that when the reaction is carried out under H₂ with tetralin present, benzyl radicals produced in the thermolysis react with H₂ to give toluene and H-atoms and that the H atoms react with DPE to give 2-phenylethyl radicals and benzene. Our earlier results are consistent with this suggestion in that the Vernon process would provoke D incorporation for the reaction under D₂. However, in our experiments, the amount of D in initially formed toluene as well as in benzene and ethylbenzene was substantially less than one atom of D per molecule demanding the conclusion that radicals present also react with DPE to give 1,2-diphenylethyl radicals. In fact, the amount of aliphatic deuterium present in unreacted DPE was quite similar to that in the formed toluene. The similarity was then explained by further experiments in which DPE-1,1-d₂ was shown to undergo extensive scrambling under the reaction conditions and that toluene-1,1,1-d₃ undergoes exchange with DPE under the reaction conditions.³ As this agreed with existing literature which provided a number of examples of exchange of H atoms between benzylic positions,⁴ it was clear that it would be difficult to identify the radical primarily responsible for removing D atoms from D₂ because the initial landing sites of D-atoms become obscured by exchange.

Although it seemed reasonable that both benzyl and 1,2-diphenylethyl radicals were capable of carrying out this reaction, the roles played by each were not separable. It seemed likely that the 1,2-diphenylethyl radical being rendered more stable by its "secondary" structure would be less reactive. On the other hand, the equilibrium between the benzyl and diphenylethyl radicals would allow the latter to accumulate in the reaction mixture for the same reason. To establish the 1,2-diphenylethyl radical as a candidate for reaction with D₂ we undertook to produce it by a route which did not also generate benzyl radicals. We thus secured 1,2,3,4-tetraphenylbutane, TPB, by a literature preparation,⁵ and undertook to study its thermolysis in the presence of D₂.

RESULTS AND DISCUSSION

1,2,3,4-Tetraphenylbutane

TPB underwent thermolytic reaction at 400 °C to give 1,2-diphenylethane, 1, and stilbene, 2, as major products. Small amounts of 1,2,3-triphenylpropane, 3, toluene, 4, and smaller amounts of benzene, 5, ethylbenzene, 6, and styrene, 7, were observed at high conversions. The product distribution is presented in Table I. It seems clear that the major reaction pathway for thermolysis of TPB is homolysis of the 2,3 bond to give two 1,2-diphenylethyl radicals, 8, which then react, predominantly, by disproportionation to give 1 and 2. Compounds 3 and 4 are presumably formed via homolysis of the 1,2 bond to give benzyl radicals, 9, and 1,2,3-triphenylprop-1-yl radicals, 10. Interestingly, the amount of 3 + 4 increases relative to 1 + 2 as the reaction progresses suggesting the possible production of some of 3 and 4 from 1 and 2. It is clear that the formation of 2 constitutes the only source of hydrogen atoms. Formation of two molecules of 1 from one TBP requires that two atoms of H be provided externally unless 2 is formed concurrently. The formation of 3 and 4 also requires a source of H or D.

As the reaction proceeds, the total moles of 1, 3, and 4 formed exceeds the moles of 2. This fact alone, in the absence of other unsaturated products, clearly predicts the consumption of D₂. Products were analyzed for deuterium content by gas chromatography/mass spectrometry (GC/MS) and, indeed, contained substantial amounts of deuterium as detailed in Table II.

Interpretation of GC/MS data obtained for recovered TPB is rendered difficult by the fact that the original molecular ion ($m/z = 362$) fragments readily to give daughter ions at ($m/z = 181$). However, the pattern of ion intensities in the $m/z = 181$ region is, within experimental error, identical to that for starting TPB suggesting that no deuterium has been incorporated. This is confirmed by ²H NMR experiments which fail to detect the presence of D atoms (upper limit of 5%). In previous experiments with more volatile substrates, we have usually found significant amounts of deuterium in all aromatic compounds present. Apparently the reaction with D atoms occurs largely in the gas phase and unreacted liquid TPB is protected in this instance by its low vapor pressure.

Most of the deuterium atoms predicted to be present are found in the diphenylethane, 1, formed. Roughly 50% of the molecules of 1 contain one or more atoms of D. Rough calculation suggests that the amount of D present in 1, plus small amounts present in other components of the reaction mixture, is sufficient to explain the excess of 1, 3, and 4 over 2. Interestingly, the stilbene present contains a relatively small amount of D. Although we have not yet been able to determine its exact location by NMR, earlier experiments suggest that this amount of D is roughly that expected for the aromatic ring exchange reaction associated with D-atom production and D-atom addition to the double bond of 2 would incorporate some D at the vinyl positions after disproportionation.

Thus, it seems clear that one-third to one-half of the 1,2-diphenylethyl radicals produced through scission of the 2,3-bond in TPB react with D₂ to give 1-d, plus a D-atom. The remainder disproportionate to give 1 plus 2. The D-atoms formed react with all gas-phase aromatic compounds to give ring exchange. We find that these results make it difficult to avoid the conclusion that 1,2-

diphenylethyl radical is a viable partner in the reaction with D_2 .

Interestingly, the small amount of toluene, 4, produced in this reaction contains about the same level of D as does 1. While we cannot say unequivocally that benzyl radicals also react with D_2 in this system, it seems unlikely that the relatively high levels of D in 4 could arise through D-atom removal from 1.

As might be expected, triphenylpropane, 3, formed also contains D. The amount is somewhat less, for reasons that are not clearly understood. One possible explanation is that the 1,2,3-triphenylprop-1-yl radical remains in the liquid phase and therefore has less ready access to gaseous D_2 .

The processes which seem likely to explain the data described are given in equations 1,2,3 and 4 in Figure 1. It will be noted that the only termination steps suggested are those in eq 2. It is clear that the amount of 2 produced is insufficient to account for all of the necessary termination processes. Whether termination reactions involving $R^{\cdot} + D^{\cdot}$ are involved or other processes must be invoked, is not clear at the present time. It will be noted that in runs to high conversion, we do not list 100% of the material balance. This is because a large assortment of minor products are formed, not all of which have been identified.

2,3-Dimethyl-2,3-diphenylbutane

From the results described above as well as those in the following paper in this series, it seemed likely that the reaction with D_2 is general for radicals of a variety of structural types. To this point the radicals studied were either monosubstituted (primary) or disubstituted (secondary). It was thus of interest to extend the scope to tertiary radicals and preliminary experiments have now been carried out with 2,3-dimethyl-2,3-diphenylbutane (bicumyl), 11. When 11 was subjected to thermolysis at 450 °C under D_2 for 30 min, the products were found to be cumene, 12, (70%) and 2-phenylpropene, 13, (30%), the latter clearly arising from disproportionation of 2-phenylprop-2-yl radical (cumyl), 14. Thus about 40% excess 12 is produced and this presumably is obtaining D from D_2 .

GC/MS studies showed that molecules of 12 were 62% d_0 , 26% d_1 and 11% d_2 . 1H and 2H NMR studies show that deuterium is being incorporated at both aliphatic positions in 12. About 55% of the aliphatic D is at the methine (CH) position and 45% is in the CH_2 groups. This suggests that when cumyl radicals react with D_2 , the D atoms produced react to a significant extent at the methylene (CH_2) group in 13, rather than at aromatic positions as observed with the diphenylethane system. The resultant deuterated cumyl radicals disproportionate and place deuterium at all positions in both 12 and 13. The sequence of events for the reaction of 11 is shown in Figure 2.

EXPERIMENTAL SECTION

Synthesis of 1,2,3,4-Tetraphenylbutane, TPB. The synthesis was carried out as described in the literature.⁵ The product was a white crystalline solid, mp 183 °C. 1H NMR δ ($CDCl_3$) 2.8 (m, 2 H), 3.1 (m, 4 H), 7.4 (m, 20 H).

Synthesis of 2,3-Dimethyl-2,3-diphenylbutane, 11. This compound was prepared by a literature procedure.⁶ The product was sublimed to give white crystals, mp 119 °C. 1H NMR δ ($CDCl_3$) 1.25 (s, 12 H), 7.10

(m, 10 H).

Thermolysis of 1,2,3,4-Tetraphenylbutane, TPB, and 2,3-Dimethyl-2,3-diphenylbutane, 11, under D₂ gas pressure. The experiments with D₂ gas were conducted in a reaction bulb with a long capillary neck described earlier.¹ Normally 100 mg of model compound was placed in the reaction vessel. The reaction products were dissolved in 0.6 mL of carbon disulfide analyzed by GC and GC-MS then separated by preparative gas chromatography. Isolated compounds were analyzed by ¹H and ²H NMR, mass spectrometry and comparison with authentic samples.

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Table I. Weight % of Products from the Thermolysis of 1,2,3,4-Tetraphenylbutane under D₂ at 400 °C.

Compound	Time (min)				
	5	10	15	20	30
TPB	92	71	41	29	16
1	2.1	16.2	22.6	26.3	33.6
2	3.5	7.4	15.2	12.4	12.7
3	0.2	3.2	3.3	11	9.6
4	<0.1	0.5	1.1	1.6	3.3
5	<0.1	0.2	0.2	--	0.4
6	<0.1	0.1	0.1	--	0.5
7	<0.1	0.1	0.1	--	0.2

Table II. Deuterium Content of Products from Thermolysis of TPB under D₂ at 400 °C.

Product	% of d _n at Time (min)				
	5	10	15	20	30
TPB-d ₀	>95	>95	>95		>95
TBP-d ₁	<5	<5	<5		<5
1-d ₀	50.5	49.8	43.8	28.6	29.8
1-d ₁	40.6	41.5	44.0	46.2	44.1
1-d ₂	8.0	7.8	10.4	20.5	20.7
1-d ₃	0.8	0.7	1.5	4.7	4.9
2-d ₀	88.0	88.5	83.1	61.6	63.0
2-d ₁	11.6	10.7	14.2	29.2	31.0
2-d ₂	0.3	0.8	1.9	6.6	6.6
3-d ₀	75	74	68		
3-d ₁	25	26	32		
4-d ₀			43.2	25.6	30.5
4-d ₁			46.2	57.7	55.3
4-d ₂			8.4	16.7	14.3

Figure 1

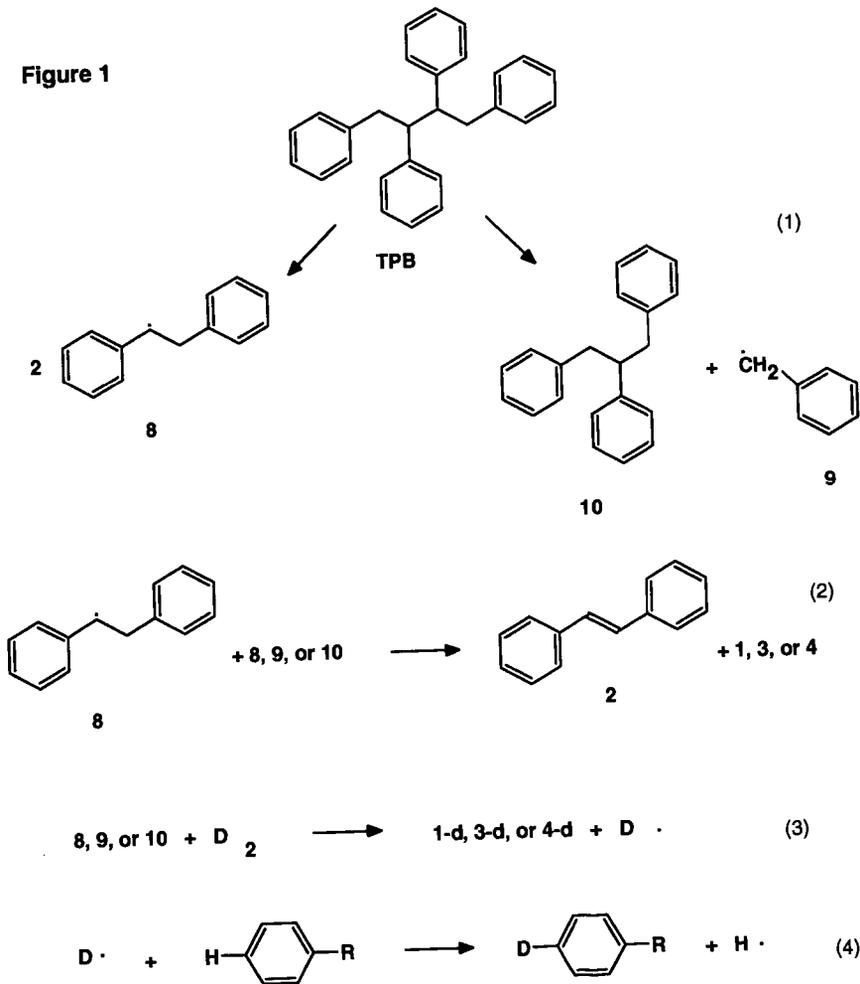
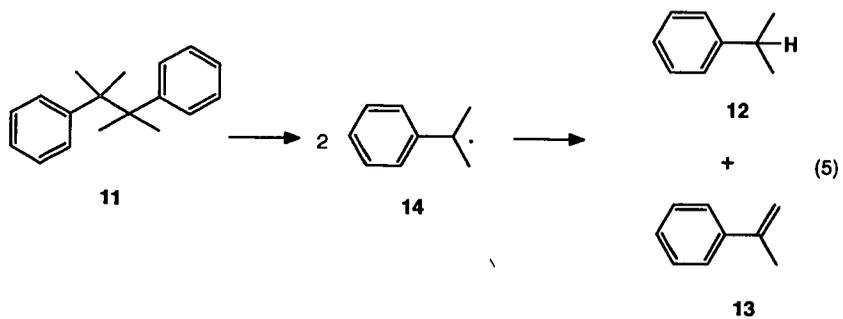


Figure 2



REACTION OF 2,2,5,5-TETRAMETHYL-3,4-DIPHENYLHEXANE
WITH D₂ AT 300-350 °C

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Keywords: radicals, liquefaction, hydrogen atoms

INTRODUCTION

In previous preprints we have described the thermolysis of 1,2-diphenylethane (bibenzyl)^{1,2} and 1,2,3,4-tetraphenylbutane under D₂.³ We have also described preliminary results with 2,3-diphenyl-2,3-dimethylbutane (bicumyl).³ In these cases the resulting pattern of deuterium incorporation into reaction products and recovered starting materials was interpreted in terms of benzylic radicals reacting with D₂ to produce D atoms which then reacted both to reverse the processes involved in their formation and also to add to unsaturated centers in the molecules present. An important mechanistic consideration for reactions of the compounds listed turned out to be the availability of a disproportionation process as the probable dominant termination step in each case. For both diphenylethane and tetraphenylbutane, a 1,2-diphenylethyl radical is formed which disproportionates to stilbene and diphenylethane. Cumyl radical can similarly give cumene and α -methylstyrene. It was thus of interest to see what might happen in a system where this option was missing. We also wished to explore temperature limitations for the reaction with D₂.

For these and other reasons, we decided to investigate the thermolysis of 2,2,5,5-tetramethyl-3,4-diphenylhexane (TMDH) under D₂. This substrate had been synthesized earlier and its thermolysis kinetics studied by Ruchardt.⁴ Thermolysis of this compound produced a rich assortment of products suggesting a complex network of reaction steps. The situation was somewhat simpler in the presence of D₂ and led to some interesting mechanistic conclusions as described below.

RESULTS AND DISCUSSION

meso-TMDH undergoes thermolysis at 300 °C, and the most abundant product after 30 min is the *d*,*l*-isomer (approx. 55 wt%). Other products are 1-phenyl-2,2-dimethylpropane (neopentylbenzene), 1, stilbene, 2, 1-phenyl-2-methylprop-1-ene,³ 2,2,4,4-tetramethyl-3-phenylpentane, 4, 1,2-diphenyl-3,3-dimethylbutane, 5, 1,1-diphenyl-3,3-dimethylbutane, 6, and other minor products. Amounts of neopentylbenzene and stilbene in the products mixture suggest the possibility of two paths for isomerization of TMDH. First by cleavage of the central C-C bond (as anticipated from the work of Ruchardt⁴) and second by cleavage of the

C-C bond between alpha and beta carbons. On further heating (at 350°C) either in vacuum or under N₂, the mixture of meso- and d,l-TMDH is completely converted to the mixture of products indicated above. The distribution of products for the reaction carried out in vacuum is given in Table I.

When the 350 °C reaction of TMDH is carried out under D₂, the proportion of neopentylbenzene in the product mixture becomes quite large: 63% as compared to 13% when run in vacuum, strongly suggesting that 1-phenylneopentyl radicals are being intercepted by D₂. It is also significant that while there is no significant amount of 1,2-diphenylethane, 7, present in the vacuum or N₂ reactions, this product develops in the D₂ reaction. The amount of stilbene, 2, formed under D₂ is smaller than the amount formed under N₂ and 7 grows in as the reaction proceeds. This suggests the possibility that 7 is formed from 2. Similarly, 1-phenyl-2-methylpropane, 8, is formed under D₂ at the expense of 3. The product 6, which is likely the rearrangement product of 1,2-diphenyl-3,3-dimethylbutyl radical, is also greatly diminished under D₂. The product distribution for the D₂ reaction is given in Table III. The results are compared graphically in Figures 1 and 2.

Mass spectrometric analysis of the major reaction product, 1, gives the results shown in Table II. Results of ¹H and ²H NMR for this compound are shown in Table IV. It will be noted that even after 5 min, at which time about 35% of the mixture of meso- and d,l-11 remains, the amount of deuterium in the 1-position of neopentylbenzene is 50% of one atom of D. The distribution does not change significantly with time. We see little alternative to the conclusion that the phenylneopentyl radical formed from dissociation of TMDH removes D from D₂ making this the clearest example so far of the reaction R[•] + D₂ → R-D + D[•]. We have no information to indicate the source of the H atoms which are required to produce the 1-d₀ produced. The most likely possibility is a termination process involving H atom removal from the tert-butyl radicals which would seem likely side products to the formation of 2, 5, and 7. The presence of compound 4 in substantial amounts in the vacuum and N₂ reactions indicate the presence of tert-butyl radicals and demonstrate the viability of a coupling with phenylneopentyl radicals. As H atom removal is an expected companion reaction to coupling, this makes the tert-butyl radical a logical source of H.

It is interesting that the level of incorporation of D in the aromatic rings of 1 and recovered TMDH is much lower relative to the aliphatic D when compared with results from the diphenylethane system. This suggests the possibility that D atoms are being scavenged by species present in the reaction mixture. A logical possibility is the 2-methylpropene expected as a product of the reaction of tert-butyl radicals with H-atom acceptors and the observance of D in the methyl groups of 4, but not of 1 confirms this suggestion. Reaction of D atoms with stilbene, 2, and 3 also seemed likely. This would seem to explain the unexpectedly high levels of D found in diphenylethane, 7, both at aromatic and aliphatic positions as shown in Table V. The possibility that stilbene can serve as an efficient scavenger for D atoms is presently under investigation. The stilbene present in the D₂ reaction was also found to contain high levels of D.

The various observations described above lead us to suggest the reaction scheme shown in Figure 3 as representing the most significant processes involved in the thermolysis of TMDH under D₂. In addition to demonstrating the viability of a number of processes having basic importance in the understanding of hydroliquefaction chemistry, this

study documents the uncatalyzed reaction of an organic compound with D₂ at an unusually low temperature.

EXPERIMENTAL SECTION

Equipment and Procedures. These have been described elsewhere.^{1,2,3}

Synthesis of 1-phenyl-2,2-dimethylpropanol. This material was synthesized by a literature method.⁵ The product was a colorless liquid, 17.5 g (53.7 %) with pleasant honey smell. ¹H NMR (CDCl₃), : 0.93 (9H, s, t-Bu); 2.65 (1H, -OH); 4.35 (1H, s, C-H); 7.3 (5H, s, -Ph).

1-Bromo-1-phenyl-2,2-dimethylpropane. This material was prepared by a literature synthesis.⁶ ¹H NMR (CDCl₃), : 1.1 (9H, s, t-Bu); 4.9 (1H, s, C-H); 7.3-7.5 (5H, m, -Ph).

meso-2,2,5,5-Tetramethyl-3,4-diphenylhexane, (1) This material was prepared by a literature synthesis.⁴ For use in the reaction with D₂ it was twice recrystallized from acetic acid, then twice from petroleum ether - stout prisms, m.p. 181 °C, ¹H NMR (CDCl₃), : 0.53 (18H, s, t-Bu); 3.05 (2H, d, -CH-); 7.15-7.3, 7.5 (10H, m, -Ph).

Thermolysis of 2,2,5,5-tetramethyl-3,4-diphenylhexane. Thermolysis of the model compound was conducted in sealed evacuated 4 mL Pyrex ampules in a silicone oil bath at 300-320 °C and in a sand bath at 330-400 °C. For each experiment 5 mg of compound was used. After pyrolysis, reaction mixture was analyzed by GC-MS.

Thermolysis of 2,2,5,5-tetramethyl-3,4-diphenylhexane under D₂ gas pressure. The experiments with D₂ gas were conducted in a reaction bulb with a long capillary neck described earlier.¹ Normally 100 mg of model compound was placed in the reaction vessel. The reaction products were dissolved in 0.6 mL of carbon disulfide analyzed by GC and GC-MS then separated by preparative gas chromatography. Isolated compounds were analyzed by ¹H and ²H NMR, mass spectrometry and, where possible, comparison with authentic samples. Details of identification will be presented elsewhere.

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Table I. Product Distribution from the Reaction of meso-TMDH at 350 °C in Vacuum.

Product	Time(min)				
	5	10	20	30	40
<u>meso</u> -TMDH	30.0	10.0	5.3	2.2	1.3
<u>d, l</u> -TMDH	37.0	16.0	6.1	2.6	2.0
1	3.7	12.7	13.6	13.2	12.9
2	4.5	11.7	12.1	12.6	12.6
3	3.5	13.0	13.3	13.6	13.8
4	3.8	11.4	12.4	12.6	12.6
5	3.4	7.0	9.1	6.1	2.0
6	6.3	10.3	12.4	8.3	3.1
7	--	--	--	--	--
8	--	--	--	--	--

Table II. Deuterium Distribution in 1-Phenyl-2,2-dimethylpropane Formed from Thermolysis of TMDH under D_2 at 350 °C (from GC/MS)

Time (min)	d_0	d_1	d_2	d_3
5	38	51	11	--
10	39	46	13	2
20	40	47	11	2
30	31	51	15	3
40	33	50	15	2

Table III. Product Distribution from the Reaction of meso-TMDH at 350 °C under D₂.

Product	Time(min)				
	5	10	20	30	40
<u>meso</u> -TMDH	16.7	2.3	1.0	0.5	0.3
<u>d,l</u> -TMDH	18.6	9.1	4.5	2.9	1.7
1	38.7	58.4	64.7	62.9	62.7
2	7.7	7.6	7.0	6.7	7.4
3	3.0	2.9	3.3	3.7	3.5
4	4.1	3.9	3.8	3.4	3.6
5	2.1	2.2	2.0	2.3	2.5
6	--	--	--	--	--
7	0.7	3.2	4.4	5.5	6.9
8	1.3	2.4	2.6	3.9	4.1

Table IV. Deuterium Incorporation in 1-Phenyl-2,2-dimethylpropane Formed from Thermolysis of TMDH under D₂ at 350 °C.

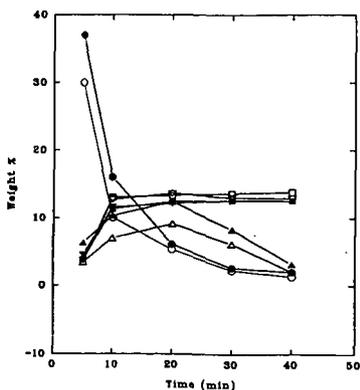
Time (min)	D/molecule (GC/MS)	D/molecule (NMR)	Aliphatic D (1-position)	Aromatic D
5	0.73	0.86	0.53	0.33
10	0.78	0.82	0.52	0.30
20	0.74			
30	0.89			
40	0.87	0.86	0.55	0.31

Table V. Deuterium Incorporation in 1,2-Diphenylethane Formed from Thermolysis of TMDH under D₂ at 350 °C.

Time (min)	D/molecule ^a (GC/MS)	D/molecule (NMR)	Aliphatic D	Aromatic D
5	2.02	2.04	0.44	1.60
10	1.95	1.98	0.67	1.31
20	2.6			
30	3.2			
40	3.3	3.37	1.55	1.82

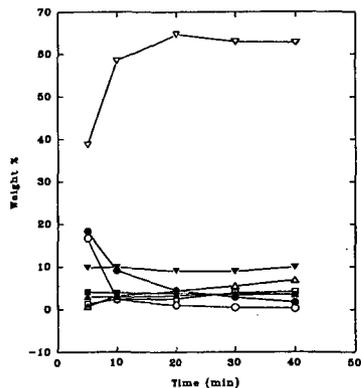
^a Because the amount of DPE formed was small, it was difficult to get reliable data. A good mass spectral analysis was produced only in the 20 min run. The distribution for this run was d₀ = 22%, d₁ = 32%, d₂ = 28%, d₃ = 13%, d₄ = 4%. The 30 and 40 min runs showed comparable distributions, but the experimental error was judged to be rather large.

Figure 1. Thermolysis of TMDH at 350 °C in Vacuum



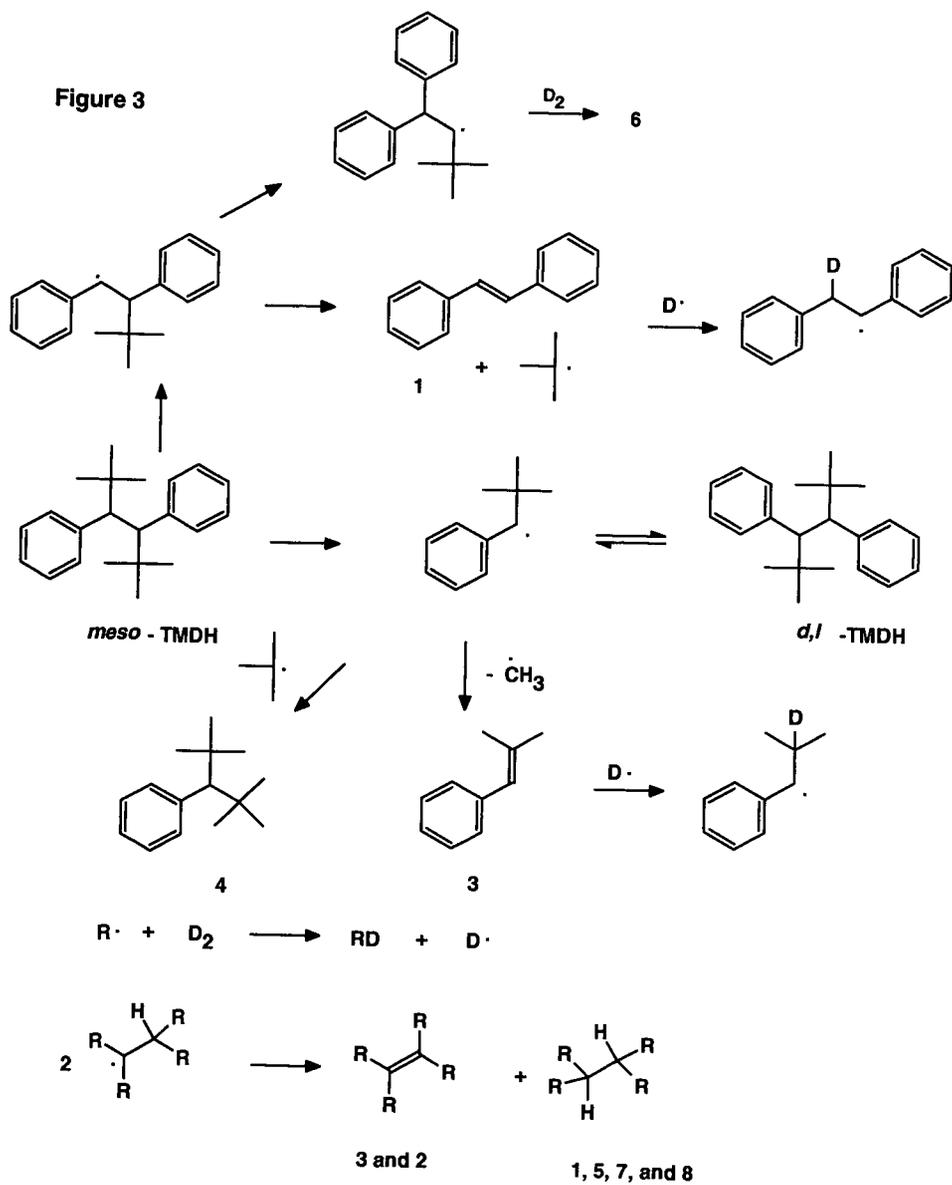
○ - m,sc-TMDH
 □ - d,l-TMDH
 ▽ - 1

Figure 2. Thermolysis of TMDH at 350 °C Under D₂



○ - m,sc-TMDH
 □ - d,l-TMDH
 ▽ - 1

Figure 3



A MECHANISM FOR SULFUR-SPECIFIC BACTERIAL DESULFURIZATION

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ABSTRACT

The desulfurization of dibenzothiophene by *Rhodococcus rhodochrous* IGTS8 was recently demonstrated to result in formation of 2-hydroxybiphenyl or of 2,2'-dihydroxybiphenyl, depending on whether growth or nongrowth conditions are used in the desulfurization experiments. The key intermediate in the bacterial degradation under nongrowth conditions is 2'-hydroxybiphenyl-2-sulfinic acid (or the corresponding cyclic sultine), which is the immediate precursor of 2-hydroxybiphenyl. Addition of either dibenzothiophene or the sulfinic acid (sultine) to pregrown cells that are using ethanol- d_6 resulted in the formation of only unlabeled 2-hydroxybiphenyl. Therefore, formation of the carbon-hydrogen bond that accompanies cleavage of the carbon-sulfur bond of the sulfinic acid was demonstrated not to require hydrogen transfer from a reducing cofactor. A mechanism consistent with proton incorporation at the ipso carbon is proposed.

Key Words: bacterial desulfurization, sulfur-specific degradation

INTRODUCTION

Because of their potential commercial use in removing sulfur from high-sulfur coals and sour crude oil, microbial systems that desulfurize organosulfur compounds have been intensively studied for several years. Some organisms utilize a catabolic pathway that results in excision of the sulfur from dibenzothiophene (DBT). Intermediates corresponding to this thiophenic-ring scission (4S) pathway have been isolated and characterized (1). Recent results obtained in feeding the various intermediates to *Rhodococcus* IGTS8 elucidated two pathways for the thiophenic scission of DBT (2). Under nongrowth conditions, the DBT is oxidized to 2'-hydroxybiphenyl-2-sulfinate 1 via the DBT 5-oxide (or the corresponding cyclic sultine ester form), and the sulfinate is subsequently cleaved to 2-hydroxybiphenyl 2 (Scheme 1). Under growth conditions, very little of the 2'-hydroxybiphenyl-2-sulfinate is converted to 2-hydroxybiphenyl, and instead most is oxidized to 2'-hydroxybiphenyl-2-sulfonate 3 (or the corresponding sultone), and 2,2'-dihydroxybiphenyl 4 is the major product. The oxidation of the sulfinate to the sulfonate occurs spontaneously (nonenzymatically) in aqueous buffer exposed to air. Further understanding of the details of the enzymes and mechanisms of the various steps in the pathways is needed.

The desulfurization of 2'-hydroxybiphenyl-2-sulfinate to 2-hydroxybiphenyl, which occurs in the last step of the *Rhodococcus* degradation of DBT under nongrowth conditions, involves replacement of the carbon-sulfur bond by a carbon-hydrogen bond. Thus the carbon appears in a reduced state in the final product, but the oxidation state of the sulfur resulting from the last step is not known with certainty. Only sulfate was found in the culture medium (2), but initially formed sulfite could have been converted to sulfate in a subsequent reaction. To elucidate the mechanism for sulfur cleavage of the sulfinate intermediate, a labeling experiment was needed to determine whether the hydrogen that is added to the carbon is

derived from a reducing cofactor, such as NADH or NADPH, or instead from a hydrogen ion derived from water.

Since ethanol is an excellent energy source for the *Rhodococcus* bacterium, deuterium-enriched ethanol was used to generate in vivo the deuterated reducing cofactor (NADH-d) that might be postulated to be involved in the carbon reduction. The 2-hydroxybiphenyl produced in this reaction was examined by mass spectrometry (MS) to determine whether a significant amount of 2-hydroxybiphenyl-2'-d was formed via a mechanism involving an addition of deuterium from the reducing cofactor. The results of the experiment can then be used to infer what kind of redox reactions occur during the last reaction of the desulfurization.

RESULTS AND DISCUSSION

Two sulfur-containing substrates (DBT and the intermediate sultine) were utilized in the desulfurization experiments with ethanol-d₆ as the energy (or potential reduction equivalent) source as well as carbon source for the cells. As expected, both substrates were converted by the bacterium *Rhodococcus rhodocrous* (ATCC #53968) to 2-hydroxybiphenyl. Gas chromatography/mass spectrometry (GC/MS) analysis of the products showed that the 2-hydroxybiphenyl produced from both substrates contained no deuterated product.

Since 2-hydroxybiphenyl-2'-d was not formed in the *Rhodococcus* desulfurization reaction of 2'-hydroxybiphenyl-2-sulfonic acid in the presence of ethanol-d₆, where reducing cofactors would have been enriched in deuterium, the mechanism of carbon-sulfur bond cleavage in the final reaction is unlikely to have occurred via transfer of a hydrogen from a reducing cofactor (as a hydride equivalent) to the ipso carbon. Thus a mechanism involving simple displacement of hydride for the sulfonyl group or a mechanism involving addition of hydride to a positive carbon intermediate cannot be used in modeling this reaction.

Thus, addition of a proton to the ipso carbon is demanded by the results, but a simple hydrolysis mechanism is not likely here. The 2'-hydroxybiphenyl-2-sulfonic acid is not hydrolytically cleaved to the aromatic compound plus sulfite in the buffered culture media. Such a cleavage of the carbon-sulfur bond would require a very strong acidic site on the enzyme that could protonate the sulfonic acid ipso ring carbon. Any very acidic site would be unstable in the buffered media. We can find no precedent for this type of enzyme activity.

The reactions of dibenzothiophenes and sulfonic acids with basic reagents have been investigated, but these studies do not appear to be applicable to the enzyme-catalyzed degradation to hydroxybiphenyl. Attack of nucleophilic oxygen has been reported to occur at the ring carbon of biphenylsulfonic acid at high temperatures in the presence of crown ether, not at the sulfur atom, resulting in the formation of 2-hydroxybiphenyl rather than biphenyl (3).

An oxidase-catalysis mechanism for the transformation of 2'-hydroxybiphenyl-2-sulfonic acid to 2-hydroxybiphenyl is the more likely alternative. The biological cleavage of aliphatic sulfoxides is known to occur via hydroxyl attack (4). Several oxidative enzymes degrade aromatics by one-electron oxidation followed by attack of hydroxide. This mechanism can produce the same intermediate, however, and the mechanism is essentially equivalent to the hydroxyl radical attack. Addition of hydroxyl radical to the arylsulfinate anion, as shown in Scheme 2, or its equivalent would result in the sulfonate radical anion 5 with substantial

anionic character in the ring. An alternative to the hydroxyl radical attack on the sulfinate sulfur is the adjacent phenol group forming the phenoxy radical 7 that adds to the sulfinate group to give the analogous cyclic sulfonate (sultone) radical anion 8. Subsequent protonation of the ipso ring carbon of either radical anion intermediate would form protonated sulfonate radical intermediates 6 or 9. In the addition reactions of the analogous sulfur ylids (sulfenes) in a hydroxylic medium, hydrogen adds to the carbon, and oxygen to the sulfur to form the sulfonate (5).

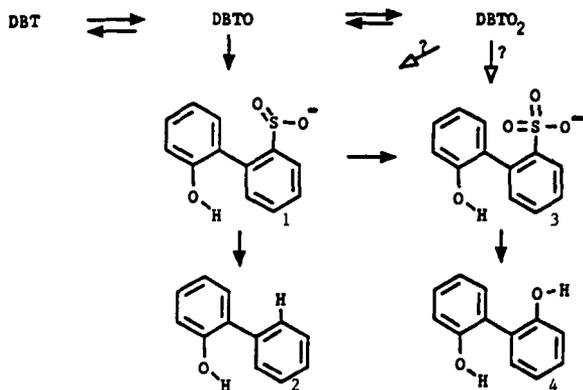
The intermediate radicals formed by this addition across the arylsulfinyl system resemble those implicated in the ipso substitution reaction investigated by Motherwell (6). In that reaction, a similar radical intermediate was formed by addition of an adjacent radical to the ipso carbon, and the sulfonyl radical was then eliminated. A similar displacement of the sulfonyl radical is proposed here in the microbial oxidase mechanism.

Depending on whether the final step involves gain or loss of an electron, either sulfite or sulfate will be formed. Or possibly disproportionation will give a mixture of the sulfite and sulfate forms. If an aryl sulfate ester forms, then an arylsulfatase enzyme may be required to complete the transformation to sulfate.

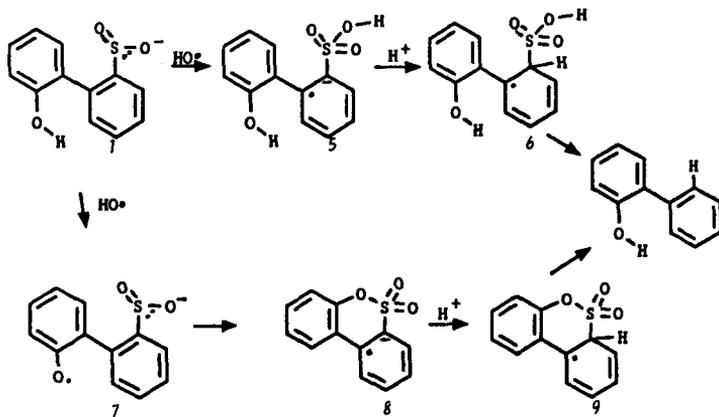
As shown in Scheme I, the reductive sulfur cleavage actually involves use of a sulfinate electron to "internally reduce" the ring carbon, the sulfinyl sulfur being converted to a sulfonate group in the process. Thus reducing cofactors are not required, as demanded by the lack of deuterium incorporation. Attack at the sulfur must be prevented in the enzyme that forms the 2-hydroxybiphenyl, or else the sulfur is simply oxidized, as it is in the formation of DBT 5-oxide and DBT 5,5-dioxide from DBT or in the formation of 2'-hydroxybiphenyl-2-sulfonic acid from 2'-hydroxybiphenyl-2-sulfinic acid.

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Scheme 1. Desulfurization Pathways in *Rhodococcus*.



Scheme 2. Mechanism of Sulfinate Desulfurization.

HYDROGENATION/DEHYDROGENATION REACTIONS OF ROSIN

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Keywords: Liquefaction, Rosin, Hydrogenation-dehydrogenation

INTRODUCTION

One of the most important factors controlling the high-temperature thermal stability of jet fuels is their chemical composition [1]. At high temperatures, pyrolysis reactions of certain components in the fuel become significant and result in the formation of gums and insoluble solids. These materials will reduce heat transfer efficiency, degrade valve performance and deposit solids in the fuel pipeline and in fuel combustor nozzles. Cycloalkanes are desirable components of advanced jet fuels because of their high thermal stability. If cycloalkanes can be produced in high yield by direct coal liquefaction, downstream processing of the product would be reduced. In order to obtain a high quality product, selection of a good feedstock is vital. Therefore, if cycloalkanes are to be produced from coal, it is reasonable to choose coals with high concentrations of these compounds already present or structures that could be easily converted to cycloalkanes.

The higher plants contain terpenoid-based substances commonly known as resins. These resins may polymerize on exposure to air, and the polymerization *in situ* in dead plants gives rise to the resinite maceral found in almost all coals. Several recent publications on resins in coal [2-6] have indicated that the resins are composed of oxidatively polymerized sesquiterpenoids and diterpenoids. Certain coals from Canada, the Far East and Australia contain diterpenoid resinites in high concentration. Western United States coals contain sesquiterpenoid resinite in high concentration (up to 5wt%) [5,6]. This paper will deal with modeling of diterpenoid resinite reactions, although the results obtained do have some relevance to sesquiterpenoid resinites. If the behavior of resinite under liquefaction conditions can be determined and understood, a highly efficient liquefaction system can be developed. Coals with high resinite concentration can be liquefied, and the cycloparaffinic products from resinite can be extracted into the oil fraction, producing liquids that are thermally stable and could be a source of high-quality jet fuel. However, because resinite is a complex mixture of polymerized compounds, it is advisable to study model compounds. This makes analysis of products easier and evaluation of reaction pathways less complicated. Rosin is commercially available and contains 90% diterpenoids (isomeric with abietic acid). In a sense, rosin is a simplified analogue of certain resinite structures and its hydrogenation-dehydrogenation behavior should give an insight into resinite liquefaction.

Because of the dwindling supply of petroleum and the possible environmental effects of fossil fuel conversion, alternative fuel sources have been sought. Biomass has emerged as a possible alternative to produce liquid fuels and chemicals. The environmental effects of the conversion of biomass should be less than those of fossil fuels. With careful process development and investigation into the chemistry of biomass conversion, the use of this renewable energy source should be realized. Tall oil is a by-product of the Kraft wood-pulping process. It contains fatty acids and rosin acids in approximately equal proportions. The use of tall oil to produce liquid fuels has been discussed in the literature [7,8] although the chemistry of the hydrocracking of the rosin acids has not been addressed. To maximize efficiency of a process to produce fuel components from tall oil or rosin, it is necessary to investigate the hydrocracking behavior of the rosin acids.

This paper will discuss the aromatisation/cracking/isomerisation reactions of rosin compounds with various catalysts. The relevance of these reactions to jet fuel production and biomass conversion will be discussed.

EXPERIMENTAL

Rosin was hydrogenated under different conditions with NiMo/Al₂O₃, Ni-Y zeolite and ammonium tetrathiomolybdate. All reactions were carried out in 25ml capacity microautoclave

reactors with cold hydrogen pressure of 7MPa. The reactors were brought to the desired temperature using a preheated sandbath. The products were analysed by GC/MS using a HP5890A GC with 5971A mass selective detector and quantified using heptadecane as an external standard.

RESULTS AND DISCUSSION

Figure 1 shows the concentration of reaction products and how they vary with temperature. At 350°C the major products of reaction are tricyclic compounds, e.g. norabietatriene. This compound is formed by decarboxylation and dehydrogenation of abietic acid (a major component of rosin). Norabietatriene is further dehydrogenated to tetrahydroretene and retene. At this low temperature, only a small amount of retene is formed. Cracking of the 3-ring compounds is minimal, with only C₄-benzene and isopropyltetralin being formed in large concentration.

At 400°C the concentration of norabietatriene increases with increasing dehydrogenation/decarboxylation of abietic acid. This increase also yields an increase in tetrahydroretene and retene in the reaction products. The concentration of alkylbenzenes triples in the products at the higher temperature. This can be accounted for by cracking of the saturated ring of isopropyltetralin seen at 350°C. The concentration of naphthalenes has not increased. This is because the temperature is not yet high enough for major cracking of the 3-ring compounds. In theory, cracking of norabietatriene will occur at the saturated terminal ring, as in hydrogenated phenanthrene, giving naphthalenes [9,10]. This does not occur at 400°C.

At 450°C naphthalenes and benzenes are now being formed. These naphthalenes are cracking products of norabietatriene, tetrahydroretene, and other partially saturated 3-ring compounds. It is unlikely that the fully aromatic retene has cracked. It is widely held that all hydrocracking reactions go in two stages: first, hydrogenation of the terminal ring and then cracking of the saturated ring [10]. Figure 1 shows the concentration of norabietatriene and tetrahydroretene decreasing after 400°C. This is in line with the thoughts that it is these compounds that are cracking to benzenes and naphthalenes, and not retene, which continues to increase.

If we interpret the chromatograms purely from the point of view of wanting to produce a good quality jet fuel, it appears that hydrocracking of the tricyclic compounds is the route to take. Naphthalenes and benzenes are produced by cracking of the diterpenes in rosin. These compounds can form the "backbone" for subsequent hydrogenation to produce desirable cycloalkanes and tetralins. Unfortunately these cracking reactions occur at high temperatures, which is accompanied by increasing dehydrogenation of the cycloparaffinic diterpenoids. In a sense, we are destroying the major property of these compounds that they were selected for — their cycloparaffinic nature. The fully aromatic retene seen in large concentration at 450°C will give rise to solid deposits in thermally stressed jet fuel. The reaction at 500°C has almost totally cracked the 3-ring compounds in rosin to naphthalenes and benzenes. Cleavage of side chains has also occurred. This may seem a good reaction if jet fuel is to be produced, but the amount of dehydrogenation makes the feasibility of this reaction being of any use small. Continuing work may prove otherwise; i.e., is it possible to re-hydrogenate the aromatic compounds to compounds that are desirable and can be hydrocracked? It is likely that in going to such a high temperature, we are simply 'going backwards to go forwards'.

Figure 2a shows how the concentrations of the products vary with reaction time for the non-catalytic run. It can be seen that cracking does not occur to a great extent until after 30 minutes. This is simultaneous with the disappearance of norabietatriene and tetrahydroretene. The concentration of retene continues to increase even as the concentration of naphthalenes increases from 0.4-3.6 mg/ml. This is further evidence that retene does not crack, although its concentration may be kept down due the fact that tetrahydroretene is being hydrocracked. To produce thermally stable cycloalkanes from diterpenoid structures, it is necessary to hydrocrack the 3-ring compounds to naphthalenes and benzenes. This needs a high temperature which also promotes dehydrogenation of cycloparaffinic compounds to unwanted fully aromatic compounds. Therefore, a two stage reaction is envisaged: 1) A high temperature cracking reaction to yield a 'backbone' of naphthalenes and benzenes. This means a reaction temperature of at least 450°C, and maybe as

high as 500°C, and a reaction time of at least 45 minutes. 2) A low temperature hydrogenation stage. The naphthalenes and benzenes from stage 1 would be catalytically hydrogenated to cycloalkanes and tetralins. The final products should fall into the jet fuel boiling range, yielding a highly thermally stable fuel.

In order to establish the optimum conditions for a temperature-staged catalytic hydrogenation, the product distribution of rosin hydrogenation was investigated using three catalysts: NiMo/Al₂O₃, Ni-Y(zeolite), and ammonium tetrathiomolybdate (ATTM).

Figure 3 shows a histogram of the product distribution of rosin hydrogenation with various catalysts (reaction temperature 400°C, reaction time 60 min.). All three of the catalysts caused a major reduction in the concentration of retene. ATTM did not crack the tricyclic compounds in rosin. In fact, it can be seen that the non-catalytic run produced more benzenes than the run with ATTM. This can be explained by the formation of dehydroabietane in the ATTM experiment. This compound is more stable than norabietatriene, due to the methyl-group substitution of the carboxyl group. Therefore, dehydroabietane does not crack and shows less tendency to dehydrogenate. Because of the low hydrocracking effectiveness of ATTM it was decided not to continue with this catalyst in this investigation. Supported NiMo shows good hydrocracking effectiveness and the Ni-Y catalyst shows an even greater cracking capability. This preliminary investigation into catalytic reactions of rosin led into a more detailed look at how product distribution would vary with time. This would help in determining the best temperature program for the two-stage reaction postulated previously.

Figure 2b shows the product distribution vs time for rosin hydrogenation with NiMo at 450°C. Three major points arise from this graph: 1) From 5-60 minutes, there is no overall increase in retene, but after 20 minutes, methylphenanthrene is formed by dehydrogenation/dealkylation of tetrahydrotetene. 2) The major cracking reactions occur after 10 minutes. Secondary cracking of naphthalenes to benzenes occurs after 20 minutes. This can be seen by the increase in concentration of benzenes after 20 minutes but naphthalenes show a 'slowing down' of formation. 3) After 40 minutes there is a maximum in the benzenes concentration. This could be explained two ways—formation of gases or coking of the catalyst. The appearance of methylphenanthrene tends to support the latter explanation but dealkylation would lead to hydrocarbon gas formation.

1-Methyl-4-isopropylbenzene (p-cymene) reaches a maximum in concentration at 40 minutes. Toluene increases slowly throughout the reaction times. The isopropyl group is quite stable but will be cleaved after 40 minutes at 450°C. This could also explain the decrease in benzenes concentration seen in Figure 2b. This is due to C₂-C₃ hydrocarbon gases being produced by cleavage of side chains. Isopropyltetralin reaches a maximum at approximately 30 minutes. The disappearance of isopropyltetralin is simultaneous with the increase in concentration of methylindene. This is due to dealkylation/isomerisation of isopropyltetralin.

As mentioned in the introduction, this work does have some application to sesquiterpenoid resinite. The proposed pathway of dealkylation to tetralin would probably occur in sesquiterpenoid structures. The isomerisation reaction could probably be controlled by tailoring the reaction temperature, and the possibility of producing tetralin is good.

Figure 2c shows the product distribution of rosin hydrogenation vs time with Ni-Y catalyst at 450°C. It can be seen that after 10 minutes of reaction, the tricyclic compounds in rosin have almost totally been cracked. Benzenes, naphthalenes and indenenes are produced in high concentration and continue to increase up to 60 minutes of reaction. Isopropyltetralin is completely dealkylated and isomerized after 60 minutes. The isomerisation reaction seems to be the major cause of loss of isopropyltetralin. This was observed with the simultaneous increase of dihydromethylindene. p-Cymene is dealkylated to toluene after 10 minutes of reaction.

In order to find a relationship between the cracking of tricyclic compounds and the appearance of mono and bicyclic compounds, a plot of the ratio of 1+2 ring to 3-ring compounds is shown in Figure 4. It can be seen that Ni-Y is the most effective hydrocracking catalyst. The maximum at 20 minutes is probably due to secondary cracking of side chains producing gases or coke formation on the catalyst. This would cause a decrease in the calculated ratio. This result also suggests a reverse-temperature-stage-program would be effective in this situation. Most of the

cracking of 3-ring compounds has taken place in the first 20 minutes at 450°C. Therefore, to continue at this high temperature would give no effective increase in the components desired for a high-quality jet fuel, and would cause excess gas formation and an increase in aromaticity.

From the above results, reaction pathways have been proposed (Scheme 1 and 2). Scheme 1 shows the dehydrogenation pathway of abietic acid in rosin. Scheme 2 deals with the possible route of cracking and isomerisation of the 3-ring compounds.

CONCLUSIONS

Diterpenoid compounds can be successfully hydrogenated and cracked to cycloalkanes and hydroaromatics using supported NiMo and Ni-Y catalysts. With careful tailoring of the process temperature and time of reaction, high quality distillate could be obtained. A reverse temperature-staged reaction with optimum conditions chosen from the plots of product distribution could yield maximum concentration of cycloalkanes and hydronaphthalenes. Fully aromatic compounds would be kept to a minimum. Diterpenoids are the most common resins in the geosphere. As well as appearing in some coal resinites, they can be found as ambers or as modern pine resins, e.g. rosin. Their chemical properties can be used in developing high quality fuels, either by direct hydrocracking or as a blending additive in a coal liquefaction process. Some of the reactions occurring in rosin hydrocracking, e.g. dealkylation and isomerisation of substituted tetralins, could be useful in determining the best way to study the liquefaction behavior of sesquiterpenoid resinites, e.g. as found in some Utah coals.

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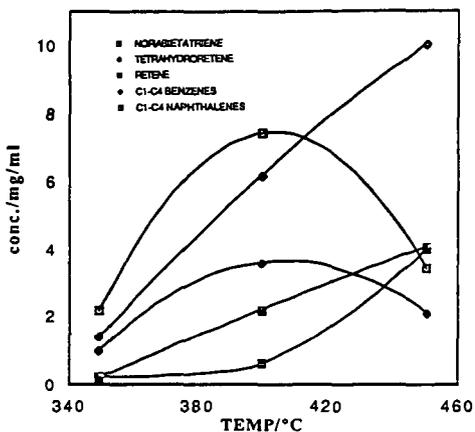


Fig.1 Concentration vs temp:no catalyst

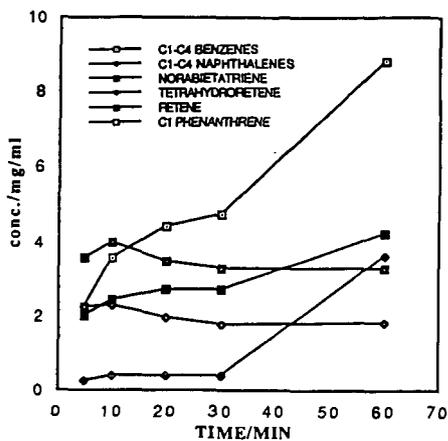


Fig.2a Concentration vs time:no catalyst

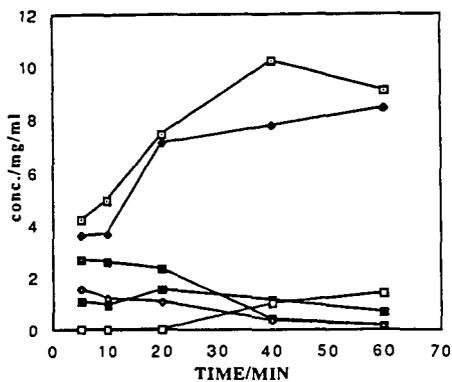


Fig.2b Concentration vs time: NiMo

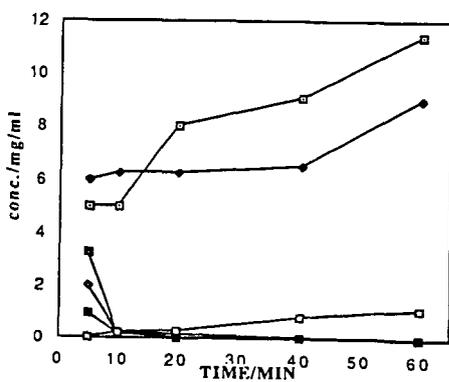


Fig.2c Concentration vs time: Ni-Y

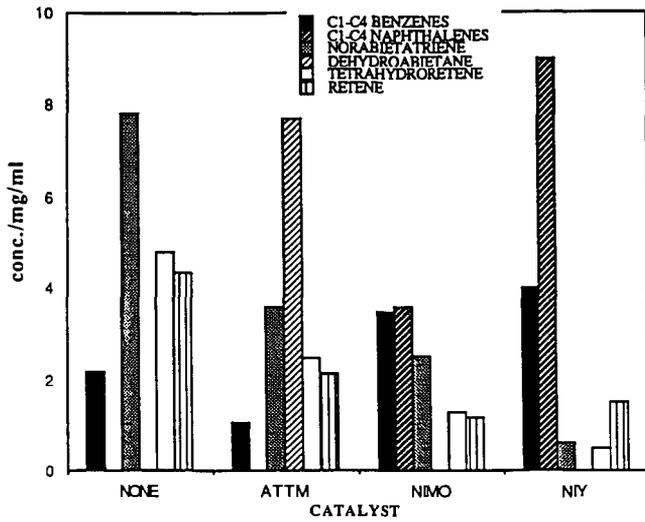


Fig.3 Concentration vs catalyst : 400°C

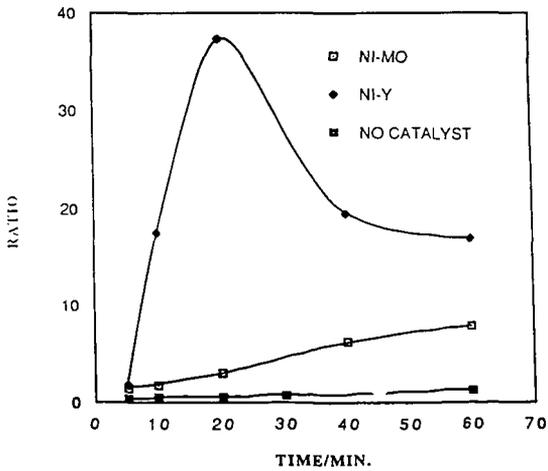
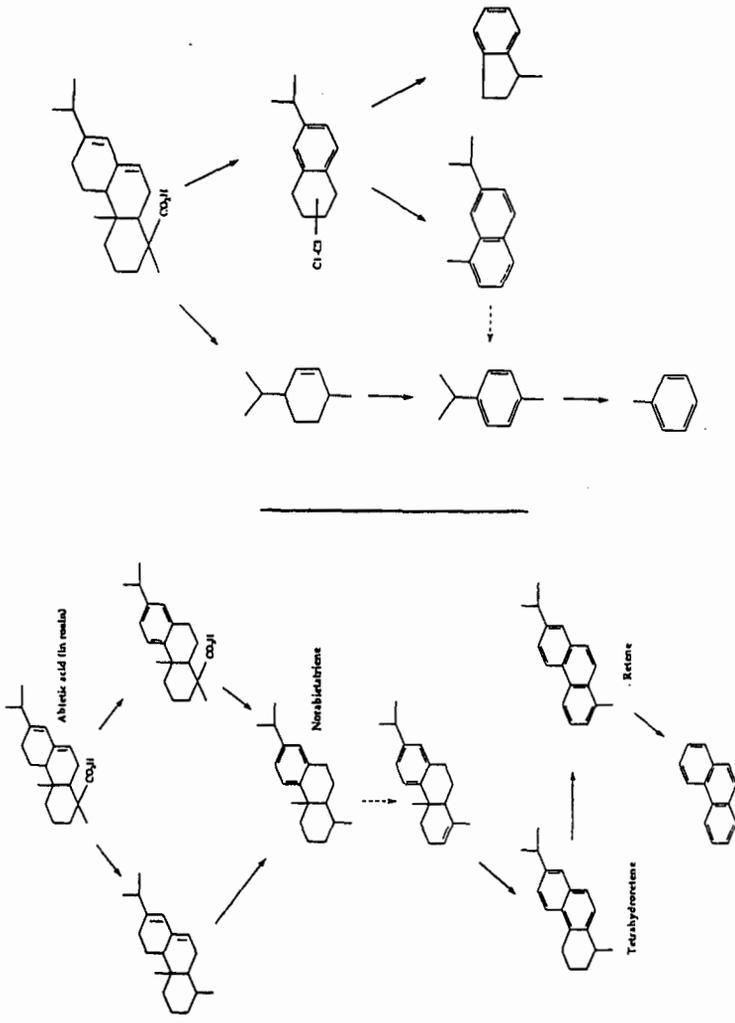


Fig.4 1+2 ring/3-ring compounds vs time



Scheme 2. Cracking/isomerisation of rosin

Scheme 1. Dehydrogenation of rosin