

COAL STRUCTURE CLEAVAGE MECHANISMS:
SCISSION OF DIPHENYLMETHANE AND DIPHENYL ETHER
LINKAGES TO HYDROXYLATED RINGS

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INTRODUCTION

Recently a number of workers¹ have subjected model compounds to various coal conversion conditions to (1) confirm that certain coal structures are reactive during coal conversion and (2) infer the conversion mechanisms of real coals from the mechanisms determined for model compounds. Thus, Collins and coworkers recently reported the results of pyrolysis of many model compounds in tetralin at 400°C.^{1a} Many, but not all, of the results can be interpreted as reactions involving straight-forward unimolecular bond-scission/radical-capping mechanisms or as radical chain reactions involving β -scissions of appropriate bonds.

In one striking and unexplained exception, Collins observed that, although diphenylmethane is for practical purposes totally unreactive in tetralin at 400°C, hydroxydiphenylmethanes (HODPM) are converted to toluene and phenol relatively rapidly, almost as fast as the weakly bonded bibenzyl reacts to form two equivalents of toluene.^{1a} This lability cannot indicate reaction by the same mode that has been shown to be operative for bibenzyl, i.e., rate-limiting bond scissions in the original model structures. Table 1 lists the estimated strengths of the weakest bonds of these HODPM compounds, estimated half-lives for unimolecular scission of these bonds, our measured half-lives, and observed products. The observed rates of conversion to phenol and toluene are faster than the estimated rates by a factor of at least 10⁶. (The good agreement between estimated and observed rates for bibenzyl indicates both the level of success expected for moderate temperature liquid-phase predictions based on high temperature gas-phase measurements, and the good agreement between the present work and the results of Miller and Stein^{1d} for a "well-behaved" system.) Oddly, the half-lives measured in our laboratory for HODPMs are 10 to 20 times longer than those of Collins, but are still very short relative to diphenylmethane. This high reactivity of the hydroxylated diphenylmethane linkage is consistent with earlier observations by Depp, Stevens, and Neuworth⁴ of the pyrolysis of 4-pyrenylmethyl-2,6-xenol, which also results in cleavage (with somewhat less specificity) of the bond between the methylene group and the aromatic ring bearing the hydroxyl group.

It is particularly significant that hydroxydiphenylmethane and hydroxydiphenyl ether structures should be susceptible to degradation by mechanisms other than those traditionally invoked in donor-solvent coal liquefactions because (1) the traditional view⁵ of coal structure is that single methylene groups and diphenyl ether structures are common coal linkages. (Recent degradation studies⁶ have provided contradictory evidence as to the importance of Ar-CH₂-Ar units in coals.); (2) bituminous coals typically possess one oxygen atom for every 20 carbon atoms, with 40% to 60% of this oxygen present as phenolic-OH;⁷ and (3) elimination of part of this oxygen is a critical and time-consuming step in donor-solvent liquefaction processes.^{1c,f}

Thus, elucidation of the mechanism(s) of conversion of these structures to lower molecular weight products in tetralin could be of significant importance to the technology of coal conversion

EXPERIMENTAL

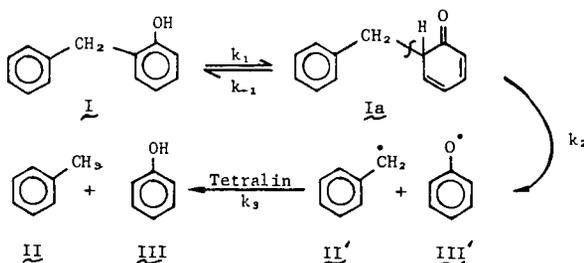
Reactions were conducted as 5 wt% solutions in 300 μ l of tetralin, in ampoules made from 4-mm fused silica tubing that had been washed in water and acetone and dried by heating under vacuum. When silanized silica surfaces were desired, they were prepared by treatment with hexamethyldisilazane vapor at 200°C for one hour. Samples were introduced and degassed by evacuation to ≤ 0.1 torr, frozen in liquid N_2 , sealed, and placed with several cubic centimeters of tetralin in steel tubes with Swagelok caps. A thermostatted molten $NaNO_3-KNO_3$ bath provided steady reaction temperatures ($\pm 0.2^\circ C$). All reactions were conducted for 21 ± 3 hours at $400 \pm 1^\circ C$. Heat-up time was < 5 minutes.

Samples for gas chromatographic analysis were prepared by dilution with tetrahydrofuran and, in some cases, addition of an internal standard to determine mass balance. Analyses were carried out on a Hewlett Packard 5711 gas chromatograph with a 1.5 m x 2 mm glass column packed with 5% OV-17 on Chromosorb W. A flame ionization detector was used. Nonlinear calibration curves were constructed for the phenolic compounds. Identification and quantification of peaks was confirmed by GC/MS and capillary GC. Mass balances ranged from 77% to 108%, usually 90% to 100%.

Most compounds were purchased from major suppliers and purified in a sublimation apparatus to $\geq 99.5\%$. Tetralin was purified by distillation using spinning band columns. The *m*-HODPM was prepared by the method of Lamartine-Balme et al.⁸ The *o*-MeODPM was prepared from basic *o*-HODPM and MeI.

RESULTS AND DISCUSSION

The most likely homogeneous mechanism for conversion of hydroxydiphenylmethanes to phenol and toluene in a hydrocarbon solvent involves a keto-enol tautomerism to produce a weakly bonded keto intermediate as shown in Scheme 1.



Scheme 1

Although the equilibrium constant for reaction (1) (k_1/k_{-1}) is $\sim 10^{-6}$ (based on estimated² enthalpy difference between the phenol and keto forms), unimolecular scission (reaction 2) of the keto-form Ia should proceed rapidly since the estimated strength² of the indicated bond is only ~ 45 kcal/mole, at least 40 kcal/mole less than any bond in the original structure (Table 1). If k_{-1} is substantially greater than k_2 , then equilibrium between the enol and keto forms will be established before homolysis, and the overall rate will be given by

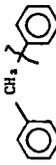
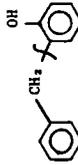
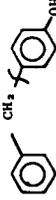
$$-\frac{d[I]}{dt} = k_{\text{obs}}[I] = \frac{k_1[I]k_2}{k_{-1} + k_2} \approx \frac{k_1}{k_{-1}}[I]k_2 \quad 1)$$

Using, as a first-order estimate of the A-factor A_2 , a value equal to that observed for bibenzyl,^{1d,2} Equation 1 results in an estimated rate constant for overall reaction of 1.5×10^{-6} , very close to our observed value of $3.3 \times 10^{-6} \text{ sec}^{-1}$ at 400°C. This agreement is consistent with reaction by the mechanism shown in Equation 1 where $k_{-1} \gg k_2$. Observed reaction rates of ortho- and para-HODPM in tetralin are listed in Table 2 as percent reaction and as defined first-order rate constants.

Table 2 also shows the rates of ortho-hydroxydiphenylmethane decomposition in the presence of several potential heterogeneous catalysts. These data indicate that (1) C-C bond cleavage in hydroxydiphenylmethanes is subject to heterogeneous catalysis by a number of surfaces, notably iron oxides, and (2) nevertheless, the observed rates of C-C bond cleavage in hydroxydiphenylmethanes, which are the principal subject of this paper, contain no significant heterogeneous component. The latter conclusion is based on findings (Table 2) that (1) rates in fused-silica and pyrex ampoules are identical, and (2) silanization of the crushed fused-silica, which was shown to be catalytically active, markedly reduces catalysis by that surface. Unless otherwise noted, reaction rates discussed in the remainder of this paper will be limited to those observed in the "normal" fused-silica ampoules in which rate-limiting steps are purely homogeneous.

Reaction via a pre-equilibrium followed by rate-limiting homolysis is additionally supported by the following observations (Table 2). First, rearrangement is observed at $\sim 10\%$ and 15% of the cleavage rates of ortho- and para-HODPM, respectively. This is consistent with solvent-caged radical recombination of structures II' and III' in Scheme 1, in which rearrangement of para-HODPM to the ortho isomer is statistically favored. The other possible recombination product, benzylphenylether, is not observed, having a half-life of less than 2 minutes at 400°C.^{1c} Second, meta-HODPM, for which no weakly bonded keto form can be drawn, is stable in tetralin at 400°C. Third, variation of ortho-HODPM concentration from 0.5 to 33.3 wt% in tetralin and variation of the extent of conversion from 3% to 22%, produced no significant changes ($> 10\%$) in the defined first-order rate constant. Thus the rate-limiting step is indeed first order in substrate. Fourth, addition of acids, bases, and a radical initiator as potential catalysts for the enol-keto equilibrium failed to cause a significant ($> 15\%$) increase in rate, in accord with the fact that acceleration of the rate at which a keto-enol pre-equilibrium is established will not affect the overall reaction rate. These catalysts were added to 4.1% ortho-HODPM in tetralin in the following amounts: phenol (2:1 mole ratio to substrate), H₂O (10:1 to 20:1), KOH (0.5:1), para-toluene-sulfonic acid (0.25:1, unstable at 400°C), diphenylether (0.2:1), and bibenzyl (0.2:1 to 1:1).

Table 1 ESTIMATED AND OBSERVED HALF-LIVES FOR BOND SCISSION OF MODEL COMPOUNDS

Model Compound	Estimated Bond Strength	Estimated $t_{1/2}^a$ at 400°C	Measured $t_{1/2}$ at 400°C	Defined First-Order Rate Constant	Principal Products in Tetralin
	89 ± 3 kcal/mole ^b	10^9 hr	> 9000 hr	$< 2 \times 10^{-8}$	None
	$\geq 86 \pm 3$ kcal/mole ^b	$\geq 10^8$ hr	58 hr	3.3×10^{-6}	 + 
	$\geq 86 \pm 3$ kcal/mole ^b	$\geq 10^8$ hr	64 hr	3.0×10^{-6}	 + 
	61.6 ± 2 kcal/mole ^c	10 hr	23 hr ^{d,e}	8.4×10^{-6}	

^aBased on estimated bond strength and an assumed A factor of $10^{13.3}$ sec⁻¹.

^bBased on values listed in References 2 and 3.

^cBased on gas-phase rate measurements and an assumed A factor of $10^{13.3}$ sec⁻¹ (Ref. 1d).

^dFrom liquid-phase measurements (present work), which give $\log k = 16.4 - [(66.3 \pm 0.3)/2.303 RT]$. (Liquid-phase measurements from Reference 1d give $\log k = 16.0 - 64.8/2.303 RT$ and $t_{1/2} = 21$ hr.)

^eData in Reference 1a indicate $t_{1/2} > 13$ hr.

^fWhen reaction is carried out in Tetralin at 400°C; units of sec⁻¹.

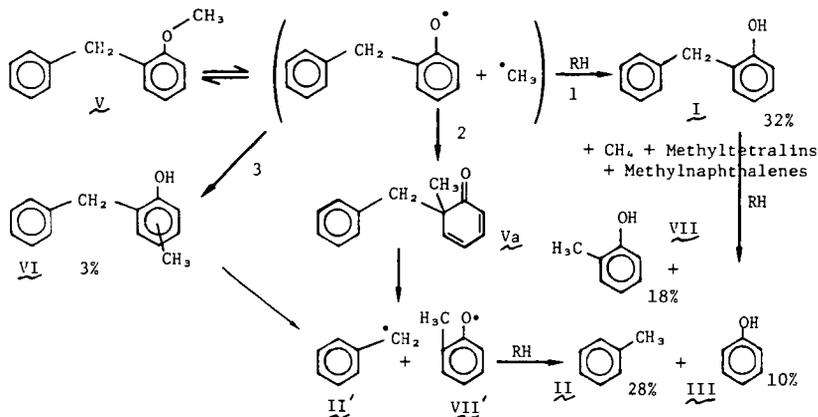
Table 2 CONVERSION OF COAL-MODEL COMPOUNDS IN TETRALIN AT 400°C IN THE PRESENCE OF HETEROGENEOUS CATALYSTS WITHOUT H₂ PRESSURE^a

Coal-Model Substrate	Wt% in Tetralin	Catalyst or Surface/Amount	% Reaction at 20 hr	k ₁ s ⁻¹ Å
o-Hydroxydiphenylmethane	4.1 (12.3 mg)	Fused-silica ampoule (normal reactor)	21	3.3 x 10 ⁻⁴
		Pyrex ampoule	21	3.3 x 10 ⁻⁴
		Silanized fused-silica ampoule	22	3.4 x 10 ⁻⁴
		Stainless steel ampoule	28	4.5 x 10 ⁻⁴
		Crushed fused-silica 0.5 g 100-200 mesh	94	3.8 x 10 ⁻³
		Silanized crushed fused-silica 0.5 g, 100-200 mesh	55	1.1 x 10 ⁻³
p-Hydroxydiphenylmethane	5.0 (15 mg)	α-Al ₂ O ₃ , 60 mg 1 μm diameter	46	8.5 x 10 ⁻⁴
		Alundum (see text) 10.4 mg 325-400 mesh ^b	36	6.3 x 10 ⁻⁴
		Crushed fused-silica 6.4 mg 325-400 mesh ^b	38	6.6 x 10 ⁻⁴
		O ₂ , 150 torr (0.12:1 mole ratio to substrate)	26	3.8 x 10 ⁻⁴
		Na ₂ Cr ₂ O ₇ , 1.5 mg	19	3.0 x 10 ⁻⁴
		Fe ₂ O ₃ , 14.8 mg 325-400 mesh ^b	61	1.3 x 10 ⁻³
m-Hydroxydiphenylmethane	5.0 (15.6 mg)	Fe ₂ O ₃ , 15 mg 0.2 μm diameter	78	2.1 x 10 ⁻³
		Fe ₃ O ₄ , 15 mg 0.2 μm diameter	≥ 99.7	≥ 8 x 10 ⁻³
		Fe ₃ O ₄ , 1.5 mg 0.2 μm diameter	58	1.2 x 10 ⁻³
		--	19	3.0 x 10 ⁻⁴
		Fe ₃ O ₄ , 15 mg 0.2 μm diameter	89	3.1 x 10 ⁻⁴
		--	~ 0	≤ 2 x 10 ⁻⁴
o-Methoxydiphenylmethane	4.1	Fe ₃ O ₄ , 15 mg/0.2 μm diameter	48	9.0 x 10 ⁻⁴
		--	90	3.2 x 10 ⁻³
		Fe ₃ O ₄ , 1.5 mg/0.2 μm diameter	94	4.0 x 10 ⁻³

^aFor the sake of comparison all rates are listed as defined first-order rate constants based on disappearance of starting material. In the case of ortho-hydroxydiphenylmethane and bibenzyl, the first-order rate constants varied by no more than 10% for 10-fold variations in concentration and 10-fold variations in extent of conversion. Mass balances (starting material plus identified products) were 97%-98% for noncatalyzed reactions, and 77%-86% for catalyzed reactions. Toluene and phenol account for ≥ 65% of the products of catalyzed reactions. The deficit in phenol and toluene was typically accounted for by 10% to 20% alkylation products and 15% to 25% high molecular weight products. The toluene/phenol ratios were typically 1.0 ± 0.2.

^bCalculated to have equal surface areas, using a spherical particle assumption and density values from Chemical Rubber Co. Handbook of Chemistry and Physics.

Additional and more direct evidence that the rate-determining step is unimolecular scission of a keto intermediate is provided by the reaction of the methyl ether of ortho-hydroxydiphenylmethane (ortho-MeODPM). Five percent ortho-MeODPM in tetralin at 400°C gave a pseudo-first-order rate constant for disappearance of substrate which is ten times greater than that observed for ortho-HODPM. The major product was ortho-HODPM, formed via the reactions proposed in Scheme 2, at a rate that is consistent with the measurements of Colussi, Zabel, and Benson⁹ and of Collins et al.¹⁰ for the rate of homolytic C-O-Et bond cleavage.

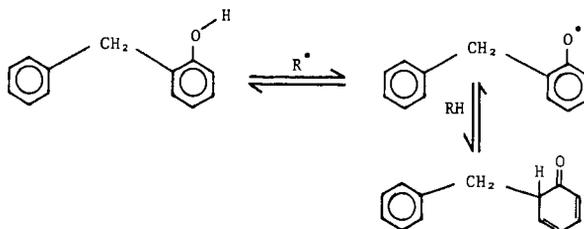


Scheme 2

The pertinent observations are (1) the total rate of formation of phenols is several times too large to be accounted for by reaction of HODPM as an intermediate, and (2) only one-third of the phenolic product is phenol; the other two-thirds is ortho-cresol. Evidently, the weakness of the Ph-Me bond provides an alternative pathway to the keto form: methyl shifts to the ortho position, either by solvent-caged radical recombination or by a symmetry hindered concerted [1,3] sigmatropic rearrangement. This shift produces an intermediate (Va) analogous to the keto tautomer in ortho-HODPM, except that in the present case establishment of a pre-equilibrium by reversal of this process is unlikely for the following reasons. There is no acidic proton to be lost in a very rapid acid-base reaction, and homolytic loss of a benzylic radical will be favored by ~ 15 kcal/mole (i.e., $> 10^4$ at 400°C) over either homolytic loss of the methyl radical,² or reversal of a [1,3] shift. Thus formation of Va leads inevitably to ortho-cresol and toluene at a rate that corresponds roughly to the rate of PhO-Me homolysis in the starting material.

Migration of the methyl group to the ring position ipso to the benzyl group seems to be fairly selective, suggested by the small amounts of VI formed. The selectivity of formation of other rearranged noncleaved products is an important factor in answering the question of whether methyl group migration is a scission-recombination process or a concerted reaction. Further details of these reactions and a discussion of this question will be presented in a subsequent publication.

The evidence presented above that the second and rate-limiting step is a unimolecular (i.e., homolytic) scission reaction provides no information about the mechanism by which tautomeric equilibrium is established. The equilibrium could be free radical in nature, as in Scheme 3, ionic, or surface catalyzed.



Scheme 3

Tautomerization by the radical chain mechanism shown in Equation 4 is plausible because tetralin is commonly observed to undergo significant rearrangement and degradation at 400°C by what have been argued to be radical chain reactions involving the 1- and 2-tetra-yl radicals,¹¹ and because exchange of benzylic hydrogens is observed with coal models even when C-C bond scission is not observed.¹² On the other hand, tautomerization by an ionic mechanism is no less likely, since deuterium exchange at the *ortho*- and *para*- positions of phenols and naphthols is reported to occur at modest rates in tetralin even at temperatures ~ 200°C lower than the temperatures used in the study.¹² In fact, subsequent measurements of the rates carbon-oxygen bond cleavage in the analogous hydroxydiphenyl ethers reveal that the fastest tautomerization process operative under the conditions of this study involve ionic reactions.

HYDROXYDIPHENYL ETHER DECOMPOSITION

The behavior of *p*-hydroxydiphenyl ether is analogous to that of *o*- and *p*-HODPM in that cleavage of the ether linkage is greatly accelerated by the presence of the hydroxy group, but differs in that the observed rate is more than two orders of magnitude too slow to result from rate-determining homolysis of the keto form. These results are illustrated in Table 3. This lack of agreement could be an indication that the general mechanism shown in Equation 1 does not apply to diphenyl ethers, or possibly even that the agreement of estimated with observed rates for the hydroxydiphenylmethanes was fortuitous. However, the results described below show that the disagreement actually results from the fact that in the case of hydroxydiphenyl ethers, tautomerization is significantly slower than it is with the HODPM. In contrast to *ortho*-hydroxydiphenylmethane decomposition, where addition of a number of different additives which would be expected to accelerate the tautomerization process failed to bring about any significant increase in the overall decomposition process (consistent with a tautomeric pre-equilibrium), the addition of KOH, *p*-cresol, or additional *p*-hydroxydiphenyl ether, all resulted in significant increases in the rate of decomposition of *p*-hydroxydiphenyl ether.

Table 3 ESTIMATED AND OBSERVED RATES OF C-O BOND SCISSION IN DIPHENYL ETHER STRUCTURES AT 400°C

Model Structure	Bond Strength, kcal/mole ^a	Est. Bond Scission Rate ^b	wt % in Tetralin	Additive wt %	Est. Rate ^c Tautomeric Equilibrium	Obs. Rate Constant, sec ⁻¹ ^d	Principal Products
	78 ± 2	5.5 x 10 ⁻¹¹	5.0	None	- - - -	~0.2 x 10 ⁻⁶	,
	78 ± 4	5 x 10 ⁻¹¹	4.7	None	4.9 x 10 ⁻³	1.7 x 10 ⁻⁶	
	78 ± 4	5 x 10 ⁻¹¹	4.7	p-cresol / 34%	4.9 x 10 ⁻³	5.5 x 10 ⁻⁶	
	78 ± 4	5 x 10 ⁻¹¹	33	(additional substrate)	4.9 x 10 ⁻³	11 x 10 ⁻⁶	
	78 ± 4	5 x 10 ⁻¹¹	4.7	KOH ^e / 1%	4.9 x 10 ⁻³	≥ 100 x 10 ⁻⁶	

^aBased on values listed in References 1d, 2, and 8.

^bExpressed as first-order rate constant, sec⁻¹; based on an assumed A-factor of 10^{15.5} sec⁻¹.

^cExpressed as first-order rate constant, sec⁻¹; calculated on the basis of Equation 2.

^dDefined first-order rate constants, k₁ = ln(C₀/C)/t.

^eHeterogeneous reaction mixture.

These results are shown in Table 3 where it can be seen that in the case of added *p*-hydroxydiphenyl ether, a 7-fold increase in substrate concentration resulted in a 5.5-fold increase in the defined first-order rate constant for decomposition. This approaches the second-order behavior expected for ionic tautomerization of phenols in tetralin.

An ionic tautomerization process that is somewhat slower in the case of hydroxydiphenyl ethers is consistent with the fact that -OR substitution is known to be deactivating for the required electrophilic attack in the ipso position.¹⁴ On the other hand, if tautomerization took place via a radical chain process, such as that shown in Equation 4, it would be difficult to rationalize such a process being significantly slower for diphenyl ether than for diphenylmethane structures.

SUMMARY AND CONCLUSIONS

The scission of strong carbon-carbon and carbon-oxygen bonds in hydroxydiphenylmethanes and diphenyl ethers during reaction in tetralin at 400°C has been shown to occur via ionic tautomerization to the respective keto forms which can undergo homolytic scission at rapid rates. In the case of the hydroxydiphenylmethanes, the tautomerization is rapid and constitutes a pre-equilibrium, but in the case of hydroxydiphenyl ethers, the tautomerization is slower and constitutes the principal rate-controlling step. Consistent with this picture, additives known to increase the rates of ring-hydrogen exchange in phenols have no effect on the decomposition rate of hydroxydiphenylmethanes, but markedly accelerate the rate of C-O bond scission in hydroxydiphenyl ethers. This latter observation suggests that the sometimes beneficial effects of added phenols in coal-conversion processes may be due, in part, to increased rates of tautomerization in diphenyl ether structures analogous to those studied in this work. Finally, an understanding of these and other details of the homogeneous decomposition mechanisms of hydroxydiphenylmethanes and hydroxydiphenyl ethers now provides a sound basis for elucidating the mechanism(s) of the facile heterogeneous cleavage that takes place in the presence of iron oxide surfaces.

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