

## Coal Structure Cleavage Mechanisms: Scission of Methylene and Ether Linkages to Hydroxylated Rings

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The kinetics of the thermolysis of the coal-model compounds (hydroxyphenyl)phenylmethanes and *p*-hydroxyphenyl phenyl ether in tetralin at 400 °C are described. The observed rates for (hydroxyphenyl)phenylmethanes are shown to be quantitatively consistent with thermochemical data and an enol-keto tautomerization followed by rate-determining homolysis of the cyclohexadienone intermediate. For *p*-hydroxyphenyl phenyl ether the breakdown of this quantitative agreement and the effects of various additives indicate that the tautomerization is rate determining and most probably involves electrophilic attack on the enolate ion. Implications for coal liquefaction and catalysis are briefly discussed.

In recent years, a number of workers<sup>1</sup> have subjected coal-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. We describe here results that elucidate the mechanism by which a certain class of coal structural models, whose reactions have been previously reported<sup>1a,hi</sup> to be unexplainedly rapid, undergo carbon-carbon and carbon-oxygen bond scissions in tetralin at 400 °C. An understanding of the general mechanism, together with known thermochemical data, has allowed us to predict the observed reaction rates with a moderate degree of accuracy in certain cases and in other cases to correctly infer a shift in rate-controlling steps.

Many of the results of previous coal-model studies<sup>1</sup> can be interpreted as reactions involving unimolecular homolytic bond-scission/radical-capping mechanisms or as radical chain reactions involving  $\beta$ -scissions of bonds. It is possible to successfully estimate the rates of such reactions through the application of gas-phase thermochemical data,<sup>2-4</sup> since such reactions do not usually demonstrate a significant change in Arrhenius behavior when conducted in nonpolar solvents. Collins and co-workers<sup>1a</sup> recently reported the results of pyrolysis of many model compounds in tetralin at 400 °C, most of which exhibit reactivities consistent with the aforementioned mechanistic pathways. Work by several laboratories<sup>1b,d,g</sup> has recently shown the thermolysis of bibenzyl to proceed via a simple bond-scission/radical-capping mechanism with a rate predictable by thermochemical techniques<sup>1d</sup> (Table I).

In one important exception, Collins et al.<sup>1a</sup> observed that, although diphenylmethane is for practical purposes totally

unreactive in tetralin at 400 °C, (hydroxyphenyl)phenylmethanes (HOPPM) are converted to toluene and phenol almost as rapidly as the weakly bonded bibenzyl reacts to form 2 equiv of toluene. As the data (present work) in Table I show, the observed reaction rates of HOPPM are too rapid by a factor of  $\sim 10^6$  to be accounted for by rate-limiting homolytic bond scissions in the original model structures, in marked contrast with the good agreement between estimated and observed rates for bibenzyl. Given the strength of the benzyl-phenyl bond in (*o*-hydroxyphenyl)phenylmethane (Table I), this lability cannot indicate reaction by the same mechanism as that invoked for bibenzyl. Paralleling the reactivity of the HOPPMs is the recently reported<sup>1h</sup> high reactivity of *p*-hydroxyphenyl phenyl ether (*p*-HOPPE) which undergoes C-O bond scission at a rate  $\sim 10^4$  times faster than expected from the known strength of the phenyl-oxygen bond (Table I).

The reactivity of this class of compounds is relevant to coal liquefaction chemistry because of the suspected prevalence of methylene and ether linkages between aromatic coal "subunits"<sup>5,6</sup> and the fact that bituminous coals typically contain one phenolic hydroxyl group for every 20 carbon atoms.<sup>7</sup> Thus, the reaction schemes presented below may account for a significant fraction of the bond breaking in thermally promoted conversions of coals to lower molecular weight, refinable products. In addition, this class of reactions is subject to homogeneous and heterogeneous catalysis, while homolyses as such are not catalyzable. Finally, elimination of oxygen from coals is a critical and time-consuming step in donor-solvent liquefaction processes.<sup>1c</sup> Thus, elucidation of the mechanism(s) of conversion of these coal models could be of importance to the technology of coal liquefaction.

### Experimental Section

Reactions were conducted as 4-5 wt % solutions in 300  $\mu$ L of tetralin in steel-jacketed, evacuated, fused-silica ampules. When desired, silanized surfaces were prepared by treatment with hexamethyldisilazane vapor at 200 °C for 1 h. Samples were introduced and degassed by evacuation to  $\leq 0.1$  torr, frozen in liquid N<sub>2</sub>, sealed, and placed with several cubic centimeters of tetralin in steel tubes with Swagelok caps. A thermostated molten

(1) (a) B. M. Benjamin, V. F. Raaen, P. H. Maupin, L. L. Brown, and C. J. Collins, *Fuel*, **57**, 269 (1978). (b) D. C. Cronauer, D. M. Jewell, K. A. Kueser, and Y. T. Shah, "Investigation of Mechanisms of Hydrogen Transfer in Coal Hydrogenation", Annual Report, July 1977, for the U.S. Energy Research and Development Administration, Contract No. E(49-18)-2305. (c) D. D. Whitehurst, M. Farcasiu, T. O. Mitchell, and J. J. Dickert, Jr., Annual Report, Feb 1977, for Electric Power Research Institute, Contract No. EPRI AF-480. (d) R. E. Miller and S. E. Stein, *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.*, **25**, 271 (1979). (e) K. R. Brower, *Fuel*, **56**, 243 (1978). (f) J. A. Franz, *Fuel*, **58**, 405 (1979). (g) M. L. Poutsma, *Fuel*, **59**, 335 (1980). (h) D. W. Carson and B. S. Ignasiak, *Fuel*, **59**, 757 (1980). (i) E. A. Depp, C. M. Stevens, and M. B. Neuworth, *Fuel*, **35**, 437 (1956).

(2) (a) S. W. Benson, "Thermochemical Kinetics", 2nd ed., Wiley, New York, 1976, p 309. (b) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, 1970.

(3) J. S. Kerr and A. F. Trotman-Dickenson in "Handbook of Chemistry and Physics", 57th ed., CRC Press, Cleveland, OH, 1976, p F-231.

(4) (a) A. J. Colussi, F. Zabel, and S. W. Benson, *Int. J. Chem. Kinet.*, **9** 161 (1977); (b) M. Rossi and D. M. Golden, *ibid.*, **11**, 715 (1979); (c) I. Szilagyi and T. Berces, *ibid.*, **2**, 199 (1970).

(5) L. A. Heredy and P. Fugassi, *Adv. Chem. Ser.*, No. 55, 448 (1968).

(6) Recent degradation studies have provided contradictory evidence as to the importance of Ar-CH<sub>2</sub>-Ar units in coal. (a) N. C. Deno, B. A. Greigger, and S. G. Stroud, *Fuel*, **57**, 455 (1978). (b) N. C. Deno, K. W. Curry, J. E. Cuyman, A. O. Jones, R. O. Minard, T. Potter, W. G. Rakitsky, and K. Wagner, *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.*, **25**, 103 (1980). (c) N. C. Deno, K. W. Curry, B. A. Grieger, A. D. Jones, W. G. Rakitsky, K. A. Smith, K. Wagner, and R. D. Minard, *Fuel*, **59**, 694 (1980).

(7) Abdel-Baset, P. H. Given, and R. F. Yarzab, *Fuel*, **57**, 95 (1978).

Table I. Estimated and Observed Half-Lives for Bond Scissions in Model Compounds

model compd <sup>g</sup>	estim bond strength <sup>a</sup>	estim $t^{1/2}$ , h (at 400 °C) <sup>b</sup>	measd $t^{1/2}$ , h (at 400 °C)	defined first-order rate constant <sup>c</sup>	principal products in tetralin
PhCH <sub>2</sub> -Ph	89 ± 3 <sup>d</sup>	10 <sup>10</sup>	>9000	≤ 2 × 10 <sup>-8</sup>	none
<i>o</i> -HOPh-CH <sub>2</sub> Ph	≥ 86 ± 3 <sup>d</sup>	≥ 10 <sup>9</sup>	58	3.3 × 10 <sup>-6</sup>	PhCH <sub>3</sub> + PhOH
<i>p</i> -HOPh-CH <sub>2</sub> Ph	≥ 86 ± 3 <sup>d</sup>	≥ 10 <sup>9</sup>	64	3.0 × 10 <sup>-6</sup>	PhCH <sub>3</sub> + PhOH
PhCH <sub>2</sub> -CH <sub>2</sub> Ph	61.6 ± 2 <sup>e</sup>	24	23 <sup>f</sup>	8.4 × 10 <sup>-6</sup>	PhCH <sub>3</sub>
Ph-OPh	78 ± 2	≥ 5 × 10 <sup>6</sup>	~1000	~ 2 × 10 <sup>-7</sup>	PhOH + phenyl-tetralin
<i>p</i> -HOPh-OPh	≥ 76 ± 3	≥ 1 × 10 <sup>6</sup>	110	1.7 × 10 <sup>-6</sup>	PhOH

<sup>a</sup>  $\Delta H_f^\circ$  300 kcal/mol. <sup>b</sup> Based on estimated bond strength and an assumed  $A$  factor of  $10^{15.5} \text{ s}^{-1}$  ( $E_{d,T} = \Delta H_d^\circ + RT \approx \Delta H_d^\circ + RT$ ). <sup>c</sup> Observed when the reaction is carried out in tetralin at 400 °C; units of  $\text{s}^{-1}$ . <sup>d</sup> Based on values listed in ref 2, 3, 4a, and 4c; 89 kcal/mol is derived from 87 and 110 kcal/mol for PhCH<sub>2</sub>-H and Ph-H bond scission, respectively. <sup>e</sup> Based on gas-phase rate measurements and an assumed  $A$  factor of  $10^{15.5} \text{ s}^{-1}$ . <sup>f</sup> From liquid-phase measurements (present work), which give  $\log k = 16.4 - [(66.3 \pm 0.3)/2.303RT]$ . (Liquid-phase measurements from ref 1d give  $\log k = 16.0 - 64.8/2.303RT$  and  $t^{1/2} = 21 \text{ h}$ ; data in ref 1a indicate  $t^{1/2} > 13 \text{ h}$ .) <sup>g</sup> The bond shown is the bond broken.

salt bath provided steady reaction temperatures ( $\pm 0.2$  °C). Reactions, except as noted, were conducted for  $20 \pm 4 \text{ h}$  at  $400 \pm 1$  °C. The heat-up time was  $< 5 \text{ min}$ . Samples for gas chromatographic analysis were prepared by dilution with tetrahydrofuran or ethyl ether and in some cases addition of an internal standard to determine mass balance. Analyses were carried out on a Hewlett-Packard 5711 gas chromatograph equipped with a flame-ionization detector and a  $1.5 \text{ m} \times 2 \text{ mm}$  glass column packed with 5% OV-17 on Chromosorb W. Nonlinear calibration curves were constructed for the phenolic compounds. Identification and quantitation of certain peaks was confirmed by GC/MS and capillary GC. Mass balance ranged from 77% to 108%, usually 90–100% in homogeneous experiments. Products more volatile than benzene were not analyzed. 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. *m*-HOPPM was prepared by the method of Lamartine-Balme et al.<sup>8</sup> *o*-MeOPPM was prepared from basic *o*-HOPPM and MeI.

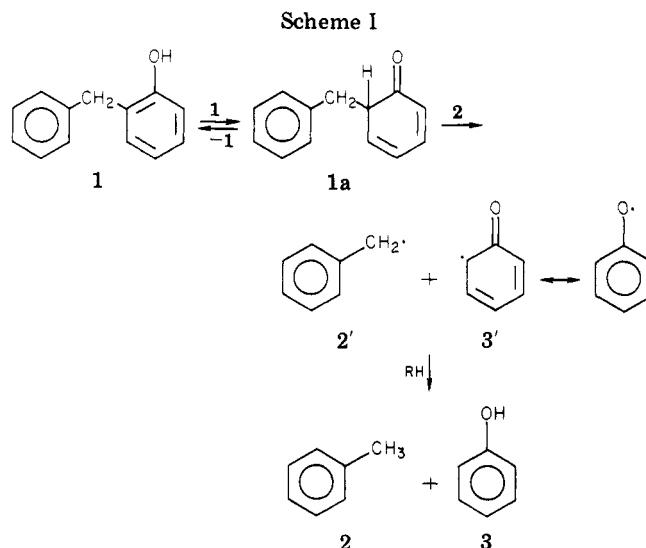
### Results and Discussion

The most likely homogeneous mechanism for conversion of (hydroxyphenyl)phenylmethanes to phenol and toluene in hydrocarbon solvent involves a keto-enol tautomerism to produce a keto intermediate (1a, Scheme I) whose benzyl-phenoxy bond at  $\sim 46 \text{ kcal/mol}$  is at least 40 kcal/mol weaker than any bond in the original structure (Table I) and can undergo rapid homolysis to give two resonance-stabilized radicals. When  $k_{-1} \gg k_2$ , the enol-keto equilibrium is established before homolysis, and the steady-state expression (eq 1) describing the overall rate

$$-\frac{d[1]}{dt} = k_{\text{obsd}}[1] = \frac{k_1[1]^2 k_2}{k_{-1}[1] + k_2} \approx \frac{k_1}{k_{-1}}[1]k_2 = \frac{k_1}{k_{-1}}[1]A_2 \exp(E_2/RT) \quad (1)$$

becomes first order in the enol form.<sup>9</sup> The equilibrium constant  $k_1/k_{-1} = [1a]/[1]$  is estimated by group additivity procedures<sup>2a</sup> to be  $\sim 10^{-6.2}$  at 400 °C. Use of this value, together with an  $A$  factor equal to that assumed for bi-benzyl (Table I) and taking  $E_2 = 47 \text{ kcal/mol}$ ,<sup>2-4</sup> results in an estimated first-order rate constant for overall disappearance of 1 of  $1.1 \times 10^{-6} \text{ s}^{-1}$ , very close to our observed values of  $3.3 \times 10^{-6}$  and  $3.0 \times 10^{-6} \text{ s}^{-1}$  at 400 °C for *o*- and *p*-HOPPM, respectively.

Additional observations (Table II) which support reaction of HOPPMs via a preequilibrium followed by rate-limiting homolysis are as follows: (1) rearrangement is



observed at  $\sim 6\%$  and  $17\%$  of the cleavage rates of *o*- and *p*-HOPPM, respectively, consistent with radical recombination of structures 2' and 3' (Scheme I); (2) *m*-HOPPM, for which no weakly bonded keto form can be drawn, is stable in tetralin at 400 °C; (3) the reaction of *o*-HOPPM is strictly first order: variation in concentration from 0.5 to 33.3 wt % in tetralin produced no significant changes ( $> \sim 10\%$ ) in the defined first-order rate constant; (4) addition of acids, bases, and a radical initiator failed to cause a significant ( $> \sim 10\%$ ) increase in rate, in accord with the fact that acceleration of the rate at which a preequilibrium is established will not affect the overall reaction rate. Variations in the character and amount of ampule surface indicate that the rate-determining steps in the experiments that provided the above observations were entirely homogeneous. Thus, these observations provide strong evidence that the homogeneous decomposition of (*o*-hydroxyphenyl)- and (*p*-hydroxyphenyl)-phenylmethane to phenol and toluene occurs by the mechanism shown in Scheme I. [Under certain other conditions (Table II), *o*-HOPPM decomposition is markedly subject to catalysis by surfaces, including materials not commonly used as acid-cracking catalysts. These latter observations will be fully discussed elsewhere.]

The mechanism in Scheme I should apply also to the reaction of the analogous hydroxyphenyl phenyl ethers. However, an attempt to use the approximate form (righthand term) of eq 1 and the appropriate thermochemical data<sup>2-4</sup> to predict the reaction rate of *p*-HOPPE results in an estimated rate that is faster by a factor of  $\sim 10^4$  than that observed; the observed rate is much too slow to be accounted for by rate-determining homolysis

(8) Lamartine-Balme et al., *C. R. Hebd. Seances Acad. Sci., Ser. C.*, 268(11), 1064-6 (1969).

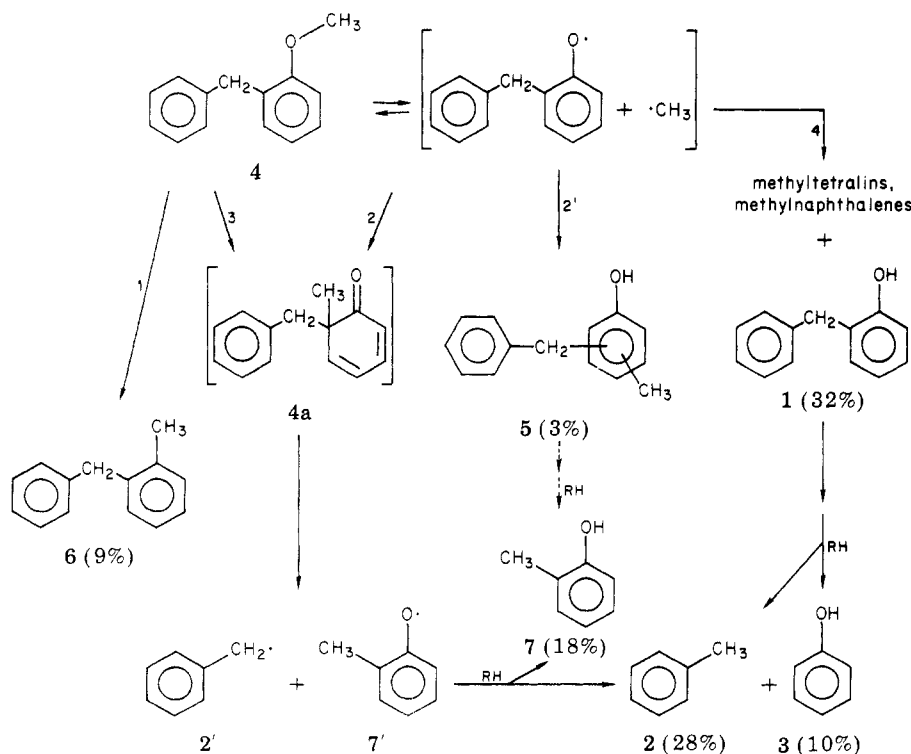
(9) Although Scheme I suggests that tautomerization is first order, it is actually second order in substrate. This fact is reflected in expression 1.

Table II. Conversion of Coal-Model Compounds in Tetralin at 400 °C<sup>a</sup>

coal-model substrate	wt % in tetralin (amt, mg)	catalyst or surface/amount	% reaction at 20 h	$k_1, s^{-1a}$	
<i>o</i> -hydroxyphenyl)phenylmethane	4.1 (12.3)	fused-silica ampule (normal reactor)	21	$3.3 \times 10^{-6}$	
		pyrex ampule	21	$3.3 \times 10^{-6}$	
		silanized fused-silica ampule	22	$3.4 \times 10^{-6}$	
		stainless-steel ampule	28	$4.5 \times 10^{-6}$	
		crushed fused-silica, 0.5 g, 100-200 mesh	94	$3.8 \times 10^{-5}$	
		silanized, crushed, fused-silica, 0.5 g, 100-200 mesh	55	$1.1 \times 10^{-5}$	
		phenol (2:1 molar ratio to substrate)	22	$3.4 \times 10^{-6}$	
		H <sub>2</sub> O (10:1 molar ratio)	21	$3.3 \times 10^{-6}$	
		H <sub>2</sub> O (20:1 molar ratio)	23	$3.7 \times 10^{-6}$	
		KOH (0.5:1 molar ratio)	23	$3.6 \times 10^{-6}$	
	5.0 (15.0)	bibenzyl (1:1 molar ratio)	22	$3.4 \times 10^{-6}$	
		no catalyst	23	$3.6 \times 10^{-6}$	
		0.41 (1.2)	no catalyst	~23	~ $3.7 \times 10^{-6}$
		O <sub>2</sub> , 150 torr (0.12:1 molar ratio to substrate)	26	$3.8 \times 10^{-6}$	
		Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> , 1.5 mg	19	$3.0 \times 10^{-6}$	
		crushed, fused-silica, 6.4 mg, 325-400 mesh <sup>b</sup>	38	$6.6 \times 10^{-6}$	
		Fe <sub>2</sub> O <sub>3</sub> , 14.8 mg, 325-400 mesh <sup>b</sup>	61	$1.3 \times 10^{-5}$	
		Fe <sub>2</sub> O <sub>3</sub> , 15 mg, 0.2- $\mu$ m diameter	78	$2.1 \times 10^{-5}$	
		Fe <sub>3</sub> O <sub>4</sub> , 15 mg, 0.2- $\mu$ m diameter	$\geq 99.7$	$\geq 8 \times 10^{-5}$	
		Fe <sub>3</sub> O <sub>4</sub> , 1.5 mg, 0.2- $\mu$ m diameter	58	$1.2 \times 10^{-5}$	
<i>p</i> -hydroxyphenyl)phenylmethane	5.0	no catalyst	19	$3.0 \times 10^{-6}$	
		Fe <sub>3</sub> O <sub>4</sub> , 15 mg, 0.2- $\mu$ m diameter	89	$3.1 \times 10^{-5}$	
<i>m</i> -hydroxyphenyl)phenylmethane	5.0 (15.0)	no catalyst	~0	$\leq 2 \times 10^{-8}$	
	5.2 (15.6)	Fe <sub>3</sub> O <sub>4</sub> , 15 mg, 0.2- $\mu$ m diameter	48	$9.0 \times 10^{-6}$	
<i>p</i> -hydroxyphenyl phenyl ether	4.7 (14.1)	no catalyst	11	$1.6 \times 10^{-6}$	
	33 (100)	no catalyst	55	$1.1 \times 10^{-5}$	
	33 (100)	4-h reaction		$7.5 \times 10^{-6}$	
	4.1 (12.3)	<i>p</i> -cresol, 34 wt % (14.6:1 molar ratio to substrate)	33	$5.5 \times 10^{-6}$	
	4.7 (14.1)	KOH, 1 wt % (0.7:1 molar ratio)	$\geq 99.95$	$\geq 1 \times 10^{-4}$	
	4.7 (14.1)	bibenzyl, 5 wt %	18	$2.7 \times 10^{-6}$	

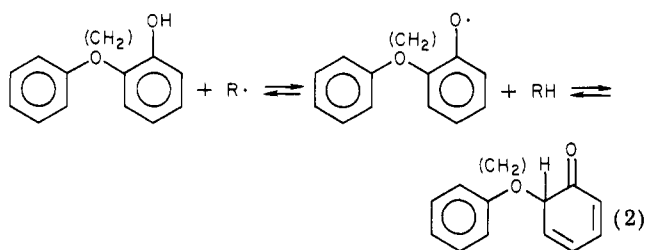
<sup>a</sup> For the sake of comparison, all rates are listed as defined first-order rate constants based on disappearance of starting material. Mass balances (starting material plus identified products) were 97-98% for noncatalyzed reactions and 77-88% for catalyzed reactions. Toluene and phenol account for  $\geq 65\%$  of the products of catalyzed reactions. The deficit in phenol and toluene was typically accounted for by 10-20% alkylation products and 15-25% high molecular weight products. For HODPM the toluene/phenol ratios were typically  $1.0 \pm 0.2$ . <sup>b</sup> Calculated to have equal surface areas by using a spherical particle assumption and nominal density values.

Scheme II

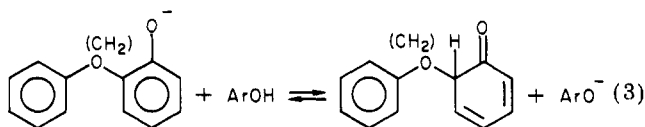


of an equilibrium concentration of the keto form. Thus, if Scheme I is valid for *p*-HOPPE, tautomerization must be slow enough to exert at least partial rate control over  $k_{\text{obsd}}$ . In contrast to *o*-HOPPM decomposition, where addition of a number of different additives known<sup>10</sup> to accelerate tautomerization failed to bring about any significant increase in the overall decomposition process, the addition of KOH, *p*-cresol, or additional *p*-HOPPE all resulted in significant increases in the defined first-order rate constant for *p*-HOPPE decomposition (Table II).<sup>11</sup> Since phenol is the reaction product, HOPPE reaction should be, and is, autocatalytic.

Acceleration of decomposition by these additives is consistent with a bimolecular, rate-limiting tautomerization. Moreover, the required tautomerization rates are of the same order as those that result from an extrapolation of the second-order ring-deuterium-scrambling rates reported by Tupitsyn and Komarov<sup>10</sup> for phenols and naphthols in tetralin at <200 °C. While the rates of radical-induced benzylic hydrogen exchange in tetralin at 400 °C reported by King and Stock<sup>12</sup> also appear to approach those necessary to provide the required tautomeric equilibrium, known radical stabilities<sup>3</sup> make it difficult to rationalize a radical chain tautomerization being significantly slower for diphenyl ether than for diphenylmethane structures (eq 2). In contrast, in the case of ionic tau-



tomization, OR substitution is known<sup>13</sup> to be deactivating for the electrophilic attack in the ipso position that is required to produce the keto form (eq 3). Thus, it is probable that an ionic bimolecular reaction such as that sketched in eq 3 is largely responsible for the enol-keto tautomerizations.



Additional evidence that the rate-determining step in the pyrolysis of HOPPM is the unimolecular scission of a keto intermediate is provided by the reaction of the methyl ether of *o*-HOPPM, (*o*-methoxyphenyl)phenyl-

methane (*o*-MeOPPM). Five percent *o*-MeOPPM in tetralin at 400 °C reacts at a rate 10 times greater than that for *o*-HOPPM (Table III). The major product is *o*-HOPPM, formed via the reactions proposed in Scheme II. The total rate of formation of monocyclic phenols is several times too large to be accounted for by reaction of HOPPM as an intermediate. Only one-third of the phenolic product is phenol; the other two-thirds is *o*-cresol. Evidently, the weakness of the phenoxy-methyl bond<sup>4a</sup> 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.<sup>14</sup> This shift produces an intermediate (**4a**) analogous to the keto tautomer in *o*-HOPPM, except that in the present case, establishment of a preequilibrium 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 (to reform an enol), and homolytic loss of a benzylic radical will be favored by ~15 kcal/mol (i.e., >10<sup>4</sup> at 400 °C) over either homolytic loss of the methyl radical<sup>12a</sup> or reversal of a [1,3] shift. Thus formation of **4a** leads inevitably to *o*-cresol and toluene.<sup>15,16,18</sup>

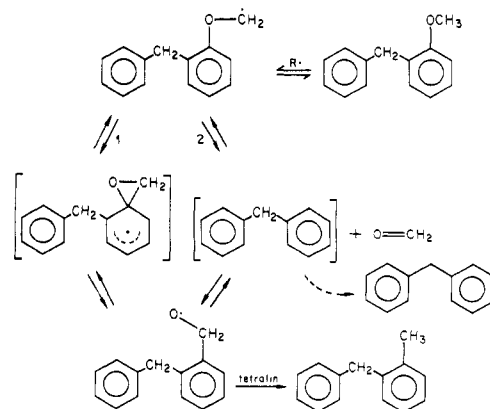
(14) A related 1,3 H shift in *o*-HOPPM is unlikely; see R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry", Academic Press, New York, 1970, p 120.

(15) Three lines of evidence implicate a concerted reaction (route 3) rather than route 2 or 2' (Scheme II) as the major pathway to cresols. First, reaction of a mixture of *o*-HOPPM and anisole resulted in no methylation of *o*-HOPPM via a cross-combination process: methyl migration is entirely intramolecular, occurring either through cage recombination or a molecular rearrangement. Second, the compounds resulting from methyl migration to positions other than ipso are present in too small a quantity (three equal GC/MS peaks, totaling 3% of products) to have acted as major intermediates in the production of cresols. Third, the *p*-cresol to *o*-cresol product ratio is only 1:36, substantially less than the 1:7 ratio observed with anisole (this work). Taken together, these observations suggest, but do not prove, that a concerted rearrangement, possibly aided by simultaneous loss of benzylic radical, provides a lower energy pathway to products.

(16) In protic solvents, acid-catalyzed rearrangements of **4a** occur at room temperature.<sup>17</sup> At the higher temperatures of this study, such rearrangement evidently cannot compete with homolysis of the benzylcyclohexadienone bond. The principal product observed by Miller (2-benzyl-6-methylphenol) is not a significant intermediate in our work.

(17) B. Miller, *J. Am. Chem. Soc.*, **92**, 6246 (1970).

(18) Formation of **6** (Scheme II) and toluene from anisole may occur through either (1) a 1,2 phenyl migration from oxygen to carbon as proposed by Collins et al.<sup>19</sup> in the phenetole/tetralin system or (2) via a functionally equivalent  $\beta$ -scission/recombination within a solvent cage. Route 1 is suggested here by the absence of (1) diphenylmethane in the reaction of *o*-MeOPPM, (2) benzene in the reaction of anisole, or (3) toluene in the reaction of *p*-methylanisole. In partial contrast to these results, Collins reported benzene as a minor but significant (12%) product of the reaction of phenetole in tetralin at 400 °C. This is consistent with a significant contribution from route 2.



(19) C. J. Collins, V. F. Reaen, B. M. Benjamin, D. H. Maupin, and W. H. Roark, *J. Am. Chem. Soc.*, **1979**, *101*, 5009.

(10) (a) I. F. Tupitsyn and V. I. Komarov, *Reakts. Sposobn. Org. Soedin.*, **6**, 616-26 (1969); (b) I. I. Kukhtenko, *Dokl. Akad. Nauk. SSSR*, **93**, 487 (1953).

(11) The addition of a radical initiator (bibenzyl) also accelerates the reaction (Table II), causing a significant but smaller increase in the HODPE decomposition rate. This is consistent with the fact that diphenyl ether itself is much more subject to radical displacement (addition-elimination) reactions than is diphenylmethane. Displacement pathways make a small contribution to C-O bond scission even in the hydroxyphenyl phenyl ether. In addition, with the increase in radical concentration, radical chain tautomerization may also provide a significant contribution to the overall reaction rate of HOPPE. These reactions will be fully discussed in a later publication.

(12) H. King and L. M. Stock, *Fuel*, **59**, 447 (1980).

(13) (a) G. A. Olah, in "Friedel-Crafts and Related Reactions", G. A. Olah, ed., Interscience, New York, 1963, p 853; (b) H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).

Table III. Conversion of Coal-Model Methoxy Compounds in Tetralin at 400 °C

coal-model substrate	wt % in tetralin (amt, mg)	% reaction at 20 h	$K_1, s^{-1} a$
( <i>o</i> -methoxyphenyl)-phenylmethane	4.1 (12.3) <sup>b</sup>	90	$3.7 \times 10^{-5}$
anisole	2.2 (6.7) <sup>b</sup>	29	$4.7 \times 10^{-6}$
<i>p</i> -methylanisole	5.0 (15.0)	64	$1.4 \times 10^{-5}$
2-benzyl-4-methylphenol	4.7 (14.1)	57	$1.2 \times 10^{-5}$

<sup>a</sup> Defined first-order rate constant based on disappearance of starting material. <sup>b</sup> Equivalent molarity in tetralin.

In summary, the scission of strong C-C and C-O bonds in (hydroxyphenyl)phenylmethanes and hydroxyphenyl phenyl 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 (hydroxyphenyl)phenylmethanes,

the tautomerization is rapid and constitutes a preequilibrium, but in the case of hydroxyphenyl phenyl ethers, the tautomerization is slower and constitutes the principal rate-controlling step. The sometimes beneficial effects of added phenols in coal conversion processes<sup>1c</sup> may be due in part to increased rates of tautomerization in diphenyl ether and diphenylmethane structures analogous to those studied in this work; the effects of added phenols may be further enhanced in coal conversions due to the inherent inhibition of bimolecular self-reactions by the coal matrix.

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**Registry No.** *o*-HOPPM, 28994-41-4; *p*-HOPPM, 101-53-1; *m*-HOPPM, 22272-48-6; *p*-HOPPE, 831-82-3; *o*-MeOPPM, 883-90-9; anisole, 100-66-3; *p*-methylanisole, 104-93-8; 2-benzyl-4-methylphenol, 716-96-1; PhCH<sub>2</sub>Ph, 101-81-5; PhOPh, 101-84-8; PhCH<sub>2</sub>CH<sub>2</sub>Ph, 103-29-7.

## Notes

### D-Homo Steroids from Oxidation of 17-Methylene Steroids by Thallium(III) Nitrate

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It is known that thallium(III) salts react with olefins and oxidative rearrangements generally occur. With thallium(III) nitrate, alicyclic olefins containing an endocyclic double bond undergo a ring contraction and ring-contracted aldehydes and ketones are obtained.<sup>1</sup> Thallium(III) perchlorate reacts with exocyclic olefins, causing a ring expansion, and the products of the oxidation are ring-enlarged ketones.<sup>2</sup> Recently, Ortar et al.,<sup>3</sup> in a study of the oxidation of a steroidal exocyclic olefin with (among other salts) thallium(III) acetate in methanol at 60 °C, obtained a ring-enlarged ketone.

This paper concerns the reaction of thallium(III) nitrate (TTN) with three 17-methylene steroids in a mixture of CH<sub>3</sub>OH/trimethyl orthoformate (TMOF) at room temperature and the characterization of the oxidation products by means of analytical and spectroscopic data.

By treating 17-methylene-5 $\alpha$ -androst-3 $\beta$ -yl acetate (1)<sup>4</sup> with TTN<sup>5</sup> in CH<sub>3</sub>OH/TMOF at room temperature, *D*-

homo-17 $\alpha$ -methoxy-17 $\alpha$ -oxo-5 $\alpha$ -androst-3 $\beta$ -yl acetate (2) is obtained.



From the chemical analysis and molecular weight (376), deduced from its mass spectrum, compound 2 has molecular formula C<sub>23</sub>H<sub>36</sub>O<sub>4</sub>. The IR spectrum exhibits an intense band at 1710 cm<sup>-1</sup>, which can be ascribed to a six-membered cyclic ketone; this band does not disappear after hydrolysis of 2 with methanolic KOH.

Compared with the spectrum of 1 (same solvent), the <sup>1</sup>H NMR spectrum of 2 shows the downfield shift of a methyl signal, the presence of a methoxy group (singlet at  $\delta$  3.40), a deshielded ethereal proton (nearly four broad signals at  $\delta$  4.07), and the disappearance of the multiplet due to methylene protons ( $\delta$  4.48). Under the same experimental conditions as for 1, TTN oxidized 17-methylene-5-androst-3 $\beta$ -yl acetate (3)<sup>4</sup> and 17-methylene-1,3,5-estratrien-3-yl acetate (5),<sup>6</sup> giving *D*-homo-17 $\alpha$ -methoxy-17 $\alpha$ -oxo-5-androst-3 $\beta$ -yl acetate (4)<sup>7</sup> and *D*-homo-17 $\alpha$ -methoxy-17 $\alpha$ -oxo-1,3,5-estratrien-3-yl acetate (6), respectively.<sup>8</sup>

The spectroscopic properties of 4 and 6 (see Experimental Section) are in good agreement with the assigned structures.

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(2) P. Abley, J. E. Byrd, and J. Halpern, *J. Am. Chem. Soc.*, **95**, 2591 (1973); D. Farcasiu and P. v. R. Schleyer, D. B. Ladlie, *J. Org. Chem.*, **38**, 3455 (1973).

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(4) G. Drefahl, K. Ponsold, and H. Schick, *Chem. Ber.*, **98**, 604 (1965).

(5) Thallium(III) nitrate has been prepared according to A. McKillop, J. D. Hunt, F. Kienzle, E. Bigham, and E. C. Taylor, *J. Am. Chem. Soc.*, **95**, 3635 (1973).

(6) Compound 5 has been prepared from 3-hydroxy-1,3,5-estratrien-17-one according to the procedure described for other 17-ketones.<sup>4</sup> Physical and spectroscopic properties of 5 are described in the Experimental Section.

(7) The 5,6 double bond does not react appreciably under these conditions with TTN.

(8) The reactions of 1, 3, and 5 with TTN give rise to complex mixtures that contain, respectively, 2, 4, and 6 as major products and many other unidentified products.