### Kinetic Study of the Thermolysis of Anisole in a Hydrogen Atmosphere

### Isabel W. C. E. Arends, Robert Louw, and Peter Mulder\*

Center for Chemistry and the Environment, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

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The gas-phase thermal decomposition of anisole diluted in a 10-fold excess of hydrogen has been studied at atmospheric pressure in a tubular flow reactor over the temperature range 793-1020 K. In the overall process the unimolecular decomposition PhOCH<sub>3</sub>  $\rightarrow$  PhO<sup>•</sup> + CH<sub>3</sub><sup>•</sup> (1) plays a prominent role. The rate constant  $k_1$  was separately determined between 790 and 875 K, employing a large (85-fold) excess of *p*-fluorotoluene as a carrier, and found to obey  $10^{15.3(\pm 0.2)} \exp[(-63.6(\pm 0.7) \text{ kcal mol}^{-1})/RT]$  (s<sup>-1</sup>). Methyl radicals formed in reaction 1 react with H<sub>2</sub> to generate highly reactive H-atoms. Induced decomposition of anisole also occurs, as the overall rate is about 1.2–1.5 times that in the toluene system. The major products are phenol and methane. Product composition and modeling studies show that the concentration of atomic hydrogen is 100 times higher when compared with the theoretical concentration in H<sub>2</sub>. The exact origin of H in the product phenol is not clear, and if combination of H<sup>•</sup> with PhO<sup>•</sup> would totally account for it (reaction 14), this rate constant must be above  $10^{11.8}$  M<sup>-1</sup> s<sup>-1</sup>. New reactions with H are advanced in order to fit product profiles through modeling with KINAL: H<sup>•</sup> + PhOCH<sub>3</sub>  $\rightarrow$  (keto)phenol + CH<sub>3</sub><sup>•</sup> for which  $k_{23}$  was set at  $10^{9.85}$  exp[(-5.4 kcal mol<sup>-1</sup>)/RT] (M<sup>-1</sup> s<sup>-1</sup>). However extra CO was formed which is not due to decomposition of phenoxyl or reactions involving the side chain conversion of anisole. Its origin is as yet unclear, but intermediately formed ketophenol is advanced as a likely candidate.

### Introduction

The stability of the phenoxyl-carbon linkage plays an important role in the thermal treatment of various biomass type molecules like lignin and coal. Depending on the chemical environment, not only the intrinsic bond strength but also the interplay with aggressive radicals determine the fate of such structures. Moreover in the recent years we have investigated the hydrogenolysis at high temperatures of a large variety of halogenated compounds, ranging from vinyl chloride up to polychlorinated biphenyls.<sup>1-7</sup> From these we know that a crucial reaction in aryl systems proves to be desubstitution of the functionalized benzene by means of H-atoms. But up to now no quantitative insight exists on how this desubstitution is effected by the presence of instable bonds. This led us to investigate the kinetics of the hydrogenolysis of methoxy substituted benzene, anisole, where both decomposition and desubstitution will occur.

In recent years several publications have appeared on the thermolysis of anisole. The main emphasis in these studies was on the kinetics of the methyl-oxygen bond dissociation (reaction 1). Experimental approaches included the toluene carrier method,

$$PhOCH_3 \rightarrow PhO^{\circ} + CH_3^{\circ}$$
 (1)

the very low pressure pyrolysis (VLPP) technique, and shock tube studies. Under these conditions the cleavage of the C–O bond appears to be the principal route of the thermal decomposition of anisole. In 1975, Paul and Back<sup>8</sup> used the toluene carrier technique to determine the rate of this bond homolysis. The production of methane, reaction 2, was measured over the

$$CH_3^{\bullet} + PhCH_3 \rightarrow CH_4 + PhCH_2^{\bullet}$$
 (2)

range 720–795 K and between 0.1 and 0.5 atm and proved to be first order in anisole:

$$k_1 = 10^{13.7} \exp[(-58.0 \text{ kcal mol}^{-1})/RT] \text{ s}^{-1}$$

Only recently Stein<sup>9</sup> used the VLPP technique, also covering the temperature range of 720–795 K. After corrections for fall-off by RRKM calculations, thereby assuming the pre-exponential factor to be identical to that calculated by  $Benson^{10}$  for the O–ethyl

bond homolysis in phenetole, the rate constant was found to obey

$$k_1 = 10^{15.5} \exp[(-63.5 \text{ kcal mol}^{-1})/RT] \text{ s}^{-1}$$

At the same time, Nelson<sup>11</sup> reported on the pyrolysis of anisole at low pressures, low concentrations, and temperatures between 850 and 1000 K. The rate of disappearance of anisole displayed first-order kinetics up to 70% decomposition, resulting in a rate constant governed by

$$k_1 = 10^{15.46} \exp[(-64.0 \text{ kcal mol}^{-1})/RT] \text{ s}^{-1}$$

Mainly cresols, accompanied by phenol, benzene, methane, and CO, were observed. They reported formation of phenol out of cresol, but the origin of the necessary H-atoms remained unclear. Anyway, the reaction pattern following the bond homolysis of anisole proved to be complex.

In addition the work done by Lin and Lin<sup>12</sup> is worth mentioning here; they studied the unimolecular decomposition of anisole in incident shock waves covering the temperature range of 1000– 1580 K (pressure range 0.4–0.9 atm). The CO formed in the reaction was monitored by resonance absorption spectroscopy. Kinetic modeling of the production of CO was based on a scheme comprising four reactions:

PhOCH<sub>3</sub> → PhO<sup>•</sup> + CH<sub>3</sub><sup>•</sup>  

$$k_1 = 1.2 \times 10^{16} \exp[(-65.8 \text{ kcal mol}^{-1})/RT] \text{ s}^{-1}$$
 (1)

PhO<sup>•</sup> → CO + C<sub>5</sub>H<sub>5</sub><sup>•</sup>  

$$k_3 = 2.5 \times 10^{11} \exp[(-43.9 \text{ kcal mol}^{-1})/RT] \text{ s}^{-1}$$
 (3)

CH<sub>3</sub><sup>•</sup> + PhO<sup>•</sup> → *o*-/*p*-CH<sub>3</sub>PhOH  

$$k_4 = 5.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$$
 (4)

$$2CH_3^{\bullet} \rightarrow C_2H_6 \qquad k_5 = 1.02 \times 10^{10} \,\mathrm{M}^{-1} \,\mathrm{s}^{-1}$$
 (5)

The rate parameters for  $k_1$  ( $A_1$  and  $E_{a1}$ ) were assessed by modeling CO yields in the very early stage of anisole decomposition for different sets of experimental data.  $A_1$  was computed from these

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Figure 1. Experimental setup, used in the pyrolysis and hydrogenolysis experiments.

data by taking a fixed value for  $E_a$  and by subsequent averaging. However,  $E_a = \Delta H^o_T - RT$ , for unimolecular processes.<sup>13</sup> This equation implicitly assumes a zero activation energy for the reverse reaction, radical recombination, when rate constants are expressed in concentration units. Therefore  $E_{a1}$  should be 61.8 instead of 65.8 at T = 1000 K (with  $\Delta H^o_1 = 63.8$  kcal/mol as applied by Lin).

Next, with use of the literature value<sup>14</sup> for  $k_5$ , the values for  $k_3$  and  $k_4$  were estimated by modeling the CO yields as a function of time according to the proposed scheme. The derived values for  $k_3$  and  $k_4$  can be questioned, not only because  $E_{a1}$  was incorrect but the value for  $k_4$  is also low when compared to a rate constant of  $1.4 \times 10^{10}$  M<sup>-1</sup> s<sup>-1</sup> for the analogous recombination of benzyl and methyl.<sup>15</sup> However the parameters for  $k_3$  have been used with success by other authors,<sup>16,17</sup> and the absolute value is in accordance with the one derived by Benson,<sup>10</sup> k\_3 = 10 s<sup>-1</sup> at 1000 K.

No previous studies have been reported on the hydrogenolysis of anisole. In our laboratory the hydrogenolysis of phenol has been investigated.<sup>16</sup> Two important pathways have been discerned, namely, benzene formation resulting from *ipso* substitution of the hydroxyl group by the H-atom (reaction 6) and formation of phenoxyl radicals through phenolic hydrogen abstraction, reaction 7.

$$H^{\bullet} + PhOH \rightarrow PhH + HO^{\bullet}$$
 (6)

$$H^{\bullet} + PhOH \rightarrow PhO^{\bullet} + H_2$$
 (7)

In this paper an analysis is presented of the various reactions in the thermolysis of anisole in a hydrogen atmosphere by studying rates and product composition as a function of temperature and modeling reaction rates. Methyl–O bond homolysis (reaction 1) was investigated separately in a 85-fold excess of p-fluorotoluene; the latter was used instead of toluene to distinguish benzene derived from toluene from that by anisole.

### **Experimental Section**

Apparatus. Experiments were performed in the apparatus outlined in Figure 1. Nitrogen carrier gas was continuously passed through an impinger filled with anisole, kept at a constant temperature. Subsequently hydrogen or p-fluorotoluene, depending on the experiment, was added to this gas mixture. Conditions are given in Table I.

The reactor was surrounded by an electrically heated furnace controlled by a proportional temperature regulator, which could be programmed in time. The temperature was measured by a chromel-alumel thermocouple situated close to the wall of the reactor. Uncertainties were  $\pm 1$  K. All flows were measured by electronic mass flow controllers. Stainless steel tubing to and from the reactor was heated to 200 °C.

**TABLE I: Experimental Conditions** 

				fle	ow (mmol/	'h)		
	temp (K)	$t_{\rm res}$ (s)	P (atm)	anisole	<i>p</i> - FPhCH₃	H <sub>2</sub>	N <sub>2</sub>	
toluene carrier	793-873	4.7	1.2	0.035	3.5		66	
hydrogenolysis	793-873	3.8	1.0	2.2		28	42	
hydrogenolysis	983-1020	0.012	1.2	1.3		47	57	

Two different types of reactors were used. The first one being a tubular quartz reactor, placed in the center of the oven (total length 140 mm). The length of the cylindrical type reactor vessel was 40 mm, with an internal diameter of 13 mm, resulting in an effective reactor volume of 5.25 mL. The kinetic character of the reactor was tested by carrying out a series of pyrolyses of ethyl acetate in nitrogen18 from 2 to 98% conversion with residence times of 2-3 s. The Arrhenius parameters derived from the observed rate constants for the unimolecular elimination of ethylene were in excellent agreement with literature when the rate equation was applied, holding for plug-flow behavior. Moreover, the temperature profile appears to be negligible (less than 5 K). In the higher temperature region (995-1030 K), a capillary quartz reactor (length 80 mm) was used with an internal diameter of 0.7 mm and total effective volume of 30.8  $\mu$ L; this reactor was also assumed to show tubular behavior. A small temperature profile might be expected in this case. Samples were taken on-line from the product stream automatically by micro-injection valves and analyzed by GC. The concentration of the reactant in the inlet gas stream was determined before each experiment by performing a blank run at 200 °C (average of 4 analyses). Products at a given temperature are determined in absolute amounts relative to the calculated amount of methane, applying the correct response factors (see analysis). Reported values are averaged from eight measurements. Methane at its turn was calculated in a separate analysis together with CO, ethylene, and ethane, on a second column relative to a calibrated amount of CO<sub>2</sub>, which was added as an external standard after the reactor.

The experiments with hexamethylethane (HME), a source of H-atoms, and cresols were performed in a more standard apparatus, as described earlier.<sup>16</sup> A solution of HME/o-cresol/p-cresol, 2 mol % each in benzene, was introduced into the system by means of an automatic syringe. This was evaporated and mixed with nitrogen and heated to 200 °C before entering the reactor (quartz tube of 20 mL). Samples were taken by trapping the outflow in a receiver cooled with liquid nitrogen. After an external standard was added, the samples were analyzed by GC.

Analytical Techniques. A Chrompack 438 gas chromatograph was used for quantitative analyses. Hydrocarbons were determined by FID on a CP-sil-5-CB (50 m  $\times$  0.32 mm i.d.) capillary column. Column conditions: gas samples (0.5 mL at 250 °C), injected at a split ratio 1:50; ultrapure N<sub>2</sub> (1.26 mL/min) carrier; temperature program, 60 °C (5 min) and 10-deg/min up to 250 °C (3 min). Quantification was based on the use of molar responses of the compounds as determined from mixtures of known composition. The relative responses in general reflect the number of carbon atoms. Identification, where necessary, was made by a HP 5890 GC equipped with MSD, using a similar capillary column and He as a carrier.

 $C_1-C_2$  products including CO and CO<sub>2</sub> were analyzed on a packed Carbosphere (80/100 mesh) column. Detection took place on a FID after methanization on a nickel catalyst (temperature 300 °C, 10 mL/min H<sub>2</sub>). Column conditions: ultrapure N<sub>2</sub> carrier gas; flow 25 mL/min; temperature program, 160 °C and 10-deg/min up to 260 °C (4 min). A standard calibrated gas mixture (Scotty II, containing 1% of CO, CH<sub>4</sub>, CO<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>) was used to determine retention times and molar responses relative to CO<sub>2</sub>.

Chemicals. Anisole, *p*-fluorotoluene, and *p*-cresol (obtained from Merck) and *o*-cresol and hexamethylethane (Janssen) were

radle n. prim	or o		vper imenits	WILL AILS	Vie						
temp (K) residence time (s)	793 4.98	803 4.92	813 4.86	823 4.80	833 4.74	843 4.68	853 4.63	858 4.60	863 4.57	868 4.55	873 4.52
					Inflow (M) <sup>4</sup>	Ь					
anisole <i>p</i> -fluorotoluene nitrogen	6.74E–6 <sup>ƒ</sup> 5.74E–4 1.79E–2	6.65E-6 5.67E-4 1.76E-2	6.57E6 5.60E4 1.74E2	6.49E-6 5.53E-4 1.72E-2	6.41È6 5.46E4 1.70E2	6.34E6 5.40E4 1.68E2	6.26E6 5.34E4 1.66E2	6.23E6 5.31E4 1.65E2	6.19E6 5.27E4 0.64E2	6.16E-6 5.24E-4 1.63E-2	6.12E-6 5.21E-4 1.62E-2
				(	Dutflow (M)	)¢					
anisole phenol methane <i>p</i> -cresol fluorobenzene <sup>d</sup> fluoroethylbenzene difluorobibenzyl difluorobibenzyl difluorobiphenyl toluene	6.53E-6 2.09E-7 3.31E-7 nd 1.34E-7 3.82E-9 nd 1.62E-7 nd 1.07E-8	6.33E-6 3.27E-7 5.03E-7 nd 2.38E-7 nd nd 2.44E-7 nd 5.52E-8	6.08E-6 4.91E-7 5.69E-7 nd 2.11E-7 nd nd 3.20E-7 nd nd	5.72E-6 7.71E-7 1.03E-6 nd 2.89E-7 nd 4.72E-7 nd 1.37E-8	5.25E-6 1.17E-6 1.52E-6 nd 4.13E-7 nd 6.99E-7 nd 3.36E-8	4.76E-6 1.58E-6 2.02E-6 9.23E-9 5.48E-7 nd 9.11E-9 1.02E-6 9.51E-9 4.18E-8	3.88E-6 2.38E-6 3.06E-6 8.78E-9 8.42E-7 nd 1.40E-8 1.55E-6 1.38E-8 1.19E-7	3.45E-6 2.78E-6 3.58E-6 1.29E-8 1.00E-6 1.79E-7 1.90E-8 1.55E-6 2.08E-8 nd	3.04E-6 3.15E-6 4.09E-6 1.75E-8 1.15E-6 nd 2.56E-8 1.77E-6 2.54E-8 1.05E-7	2.39E-6 3.76E-6 4.95E-6 1.81E-8 1.53E-6 nd 3.99E-8 2.45E-6 3.06E-8 nd	2.03E-6 4.09E-6 5.41E-6 2.10E-8 1.65E-6 3.56E-7 4.21E-8 2.25E-6 3.61E-8 1.96E-7
				Percenta	ge on Intake	e Anisole <sup>e</sup>					
anisole phenol methane	96.90 3.10 4.91	95.09 4.91 7.55	92.53 7.47 8.65	88.12 11.88 15.80	81.80 18.20 23.62	75.14 24.86 31.81	61.95 38.05 48.82	55.43 44.57 57.43	49.14 50.86 66.07	38.88 61.12 80.46	33.22 66.78 88.38
CH4-PhF/PhOH	0.94	0.81	0.73	0.95	0.94	0.93	0.93	0.93	0.93	0.91	0.92

TABLE II: *p*-Fluorotoluene Carrier Experiments with Anisole<sup>a</sup>

<sup>a</sup> Concentrations are given at 1.2 atm and the applied reaction temperature. For the experiments a tubular reactor of 5.25 mL was used. Outflow is calculated with anisole (in) = anisole (out) + phenol (out) + cresole (out); this assumption was justified because no accurate anisole inflow could be calculated due to the lack of internal standard and because the rough O-balance ranged from 90 to 103%. <sup>b</sup> Intake anisole 0.025 mmol/h, excess *p*-fluorotoluene = 85. <sup>c</sup> Not detected (nd) products are below integration level (1E-9 M). <sup>d</sup> Yield corrected for small percentage already present in fluorotoluene as such. <sup>e</sup> Yield corrected for anisole + phenol always being 100%. <sup>f</sup> Where 6.74E-6 is 6.74 × 10<sup>-6</sup>.



Figure 2. Pyrolysis of *p*-fluorotoluene: yields of anisole, methane, and phenol (expressed as mole percent of initial anisole intake) as a function of temperature.

analyzed as >99.5% pure by GC. Tank hydrogen and nitrogen (Hoekloos) were used as such.

Modeling Experiments. The program package KINAL<sup>19</sup> was used to evaluate a reaction mechanism of 24 reactions and 21 species and contains 4 modules. The *DIFF* module solves the differential equations governed by the reactions that are used to describe the system. *SENS* computes the local (first-order) concentration sensitivity matrix. *PROC* generates the rate sensitivity matrix from concentration data or uses matrix computed by SENS and extracts the kinetic information by principal component analysis. *YRED*, finally, provides hints for the elimination of species.

However, apart from DIFF, the only module used in this article was PROC, which sufficed to evaluate sensitivities.

The calculations were performed on a PC equipped with a 80486 processor. Typically the calculation time was around 20 s.

#### Results

1. Experiments with *p*-Fluorotoluene. To verify the kinetics of the bond homolysis (reaction 1), anisole has been pyrolyzed in a 85-fold excess of *p*-fluorotoluene between 790 and 875 K, with nitrogen as a carrier gas, at 1.2 atm of total pressure. The residence time was ca. 4.7 s, and the degree of conversion ranged

from 3 to 67%. Main products are phenol, methane, and difluorobibenzyl; the yield of methane was always larger than that of phenol (Figure 2).

Apart from phenol and methane, a number of *p*-fluorotoluene derived products have been detected and quantified (Table II).

As denoted in ref 8, in the toluene carrier technique radicals produced in reaction 1 are scavenged by toluene and replaced by the unreactive benzyl radicals, in this case fluorobenzyl radicals. These radicals recombine mainly to give difluorobibenzyl.

$$CH_3^{\bullet} + FPhCH_3 \rightarrow CH_4 + FPhCH_2^{\bullet}$$
 (8)

$$PhO' + FPhCH_3 \rightarrow PhOH + FPhCH_2^{*}$$
 (9)

$$2FPhCH_2^{\bullet} \rightarrow FPhCH_2CH_2PhF$$
(10)

The sum of the remaining anisole and the products of phenol and traces of cresols yields a mass balance of essentially 100% over the temperature range employed. An Arrhenius plot for first-order rate constants based on phenol formation was constructed (Figure 3) and has the following parameters:

$$k_1 = 10^{15.3(\pm 0.2)} \exp[(-63.6(\pm 0.7) \text{ kcal mol}^{-1})/RT] \text{ s}^{-1}$$

Unlike VLPP, no pressure corrections are needed.<sup>20</sup> And the very good agreement with the data in refs 9 and 11, as illustrated in Figure 3, substantiates the assumption that reactions are at the high-pressure limit. The calculated A-factor is in accord with this type of unimolecular reaction.<sup>21</sup> From the activation energy the heat of formation of the phenoxyl radical can be derived as 12.1 kcal/mol (see Appendix A).

We conclude that under our conditions the toluene carrier method is capable of measuring accurate rate constants even at high degrees of conversion (up to 70%) at atmospheric pressure.

A full discussion of the chemistry of p-fluorotoluene—triggered by anisole decomposition—is beyond the scope of this paper, but some salient features should be pointed out. The methane/phenol product ratio—ideally 1—is well above unity. The excess of methane closely corresponds to the amount of fluorobenzene which



Figure 3. Arrhenius plot for anisole homolysis in *p*-fluorotoluene: ( $\Box$ ) this study with regression line,  $\log(k/s^{-1}) = (15.3-63.6 \text{ kcal mol}^{-1})/2.3RT$ ; (--) data from Back,<sup>8</sup>  $\log(k/s^{-1}) = (13.7-58.0 \text{ kcal mol}^{-1})/2.3RT$ ; (--) data from Stein,<sup>9</sup>  $\log(k/s^{-1}) = (15.5-63.5 \text{ kcal mol}^{-1})/2.3RT$ ; (--) data from Nelson,<sup>11</sup>  $\log(k/s^{-1}) = (15.46-64.0 \text{ kcal mol}^{-1})/2.3RT$ .

### SCHEME I: H Release from Recombination Reactions of Benzyl Radicals



must have been produced through demethylation of fluorotoluene with H-atoms:

$$H^{\bullet} + FPhCH_3 \rightarrow FPhH + CH_3^{\bullet}$$
(11)

The necessary H-atoms may be produced as depicted in Scheme I. In the first route a H-atom is abstracted from bibenzyl by probably benzyl radicals (which is a slow process), to give an 1,2-diphenylethyl radical. This radical can either return to bibenzyl through reaction with toluene or loose its hydrogen to give stilbene; the latter is actually detected as a product. In route II the H-atom is produced directly, accompanied by some stabilized soot precursor radical.<sup>22</sup> This route was introduced to account for the significant production of fluorobenzene as well as toluene. Formation of toluene is likely to proceed through *direct* F-abstraction by H to form HF.<sup>6</sup> The corresponding rate constant at 823 K is 11 times slower than for removal of methyl by an H-addition/elimination proces; our product ratio fluorobenzene/toluene of 12.5 at 793 K and 8.4 at 873 K shows that these processes are indeed operative.

Stilbene production is almost 200 times slower than that of fluorobenzene, and route I (Scheme I) is therefore of minor importance. The rates for the reactions in Scheme I are not known, but the degree of conversion of *p*-fluorotoluene into fluorobenzene is very small, typically 0.1%, and still less than 0.3% at the highest temperature. As anisole will also react with H<sup>•</sup> at a comparable rate, induced decomposition of anisole through H<sup>•</sup> is insignificant. Logically CH<sub>3</sub><sup>•</sup> and FPhCH<sub>2</sub><sup>•</sup> radicals are more prominently present, but are equally unable to engender anisole conversion (concentrations calculated in Appendix B). With [CH<sub>3</sub><sup>•</sup>] =  $2 \times 10^{-10}$  M and  $k_{12} = 1 \times 10^6$  M<sup>-1</sup> s<sup>-1</sup> at 873 K<sup>23</sup>, only ca. 0.04% of anisole will react like this at the upper end of the temperature region.

$$CH_3^* + PhOCH_3 \rightarrow CH_4 + PhOCH_2^*$$
 (12)

And, although [FPhCH<sub>2</sub><sup>•</sup>] is ca.  $2 \times 10^{-8}$  M at 873 K (Appendix



Figure 4. Anisole pyrolysis in a hydrogen atmosphere: yields of methane and phenol (expressed as mole percent of initial anisole intake) as a function of temperature. Low-temperature region,  $t_{res} = 3.8$  s; hightemperature region,  $t_{res} = 0.012$  s.

B), its endothermic reaction with anisole will be slow (probably  $k \approx 4 \times 10^4 \,\mathrm{M^{-1}\,s^{-1}}$ , analogous to that for H-transfer from toluene to benzyl<sup>24</sup>) and therefore equally unimportant.

2. Thermolysis in Hydrogen. Hydrogenolysis of anisole was performed in two temperature ranges, 793–873 and 983–1020 K, employing different reactors. For three temperatures in the lower region, two different concentrations were applied (see Table III). The results for the high-temperature range are given in Table IV.

Main products are phenol, methane, CO, and benzene and some minor products: benzaldehyde, o-/p-cresol, cyclopentadiene, ethane, ethylene, toluene, and dibenzofuran. Traces of 2,2'dihydroxybiphenyl were also found. No acetaldehyde or ethoxybenzene was detected, in accordance with ref 11. The oxygen mass balance was close to 100% at all temperatures.

When the rates of disappearance in  $H_2$  are compared with those found for the fluorotoluene system (vide supra), hydrogenolysis is roughly twice as fast at 823 K, entailing that about equal quantities of anisole react via primary dissociation (reaction 1) and by induced decomposition. Over the temperature range studied, the contribution of reaction 1 in the overall disappearance increases from 8% at the lowest to 88% at the highest temperature studied.

Phenol and methane will primarily arise via reactions 13–15, respectively, following bond homolysis (1). Again, the yield of

$$PhO^{\bullet} + H_2 \rightarrow PhOH + H^{\bullet}$$
 (13)

$$PhO^{*} + H^{*} \rightarrow PhOH$$
 (14)

$$CH_3^* + H_2 \rightarrow CH_4 + H^*$$
(15)

methane is higher than that of phenol (see Figure 4), but now this is due to alternative reactions of PhO<sup>•</sup>, presumably decomposition into CO and cyclopentadienyl<sup>12</sup> (reaction 3) and recombination to give 2,2'-dihydroxybiphenyl and dibenzofuran (DBF)<sup>25</sup> (reaction 16). Furthermore phenol is likely to undergo

$$hO^{\bullet} \longrightarrow CO + C_{5}H_{5}^{\bullet}$$
(3)

$$2PhO^{\circ} \longrightarrow o HO - PhPh - o OH \xrightarrow{H^{\circ}} OBF + OH^{\circ} (16)$$
$$H_{2}^{\circ}$$

$$PhOH + H^{\bullet} \longrightarrow PhH + {}^{\bullet}OH$$
(6)

hydrodehydroxylation,<sup>16</sup> reaction 6. The latter reactions lead to water via  $\cdot OH + H_2 \rightarrow H_2O + H^{\circ}$  and a concomitant loss of

TABLE III:	Hydrogenoly	sis of	Anisole in	the Low-	-Temperature	Region <sup>a</sup>
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INDER III. II.	an offenting	313 UI AIII	sole m th		mperature	Region						
temp (K) residence time (s)	793 3.90	803 3.86	813 3.81	823 3.77	833 3.72	843 3.69	853 3.64	863 3.61	873 3.56	853 3.89	863 3.85	873 3.80
Inflow (M) <sup>b</sup>												
anisole hydrogen nitrogen	5.05E-4 <sup>e</sup> 6.13E-3 9.23E-3	4.74E4 6.06E-3 9.12E-3	4.83E-4 5.98E-3 9.01E-3	4.49E-4 5.91E-3 8 90E-3	4.49E-4 5.84E-3 8.79E-3	4.15E-4 5.77E-3 8.69E-3	4.30E-4 5.70E-3 8.58E-3	3.83E-4 5.64E-3 8.48E-3	4.16E-4 5.57E-3 8.39E-3	4.22E-5 5.99E-3 8.25E-3	4.59E-5 5.92E-3 8.15E-3	4.74E-5 5.85E-3 8.06E-3
intro Son	<i>).232-3</i>	J.12L-J	7.01E-5	0.701-5	0.771-5	() () ()	0.501-5	0.401-5	0.376-3	0.252-5	0.156-5	0.00L-J
		4.945.4	4.1 CT 4	a ((E) 4	Outric	SW (M) <sup>€</sup>	A 465 4	1.005.4	1 485 4			
anisole	4.05E-4	4.24E-4	4.13E-4	3.00E-4	3.34E-4	2./SE-4	2.45E-4	1.82E-4	1.47E-4	2.0/E-5	1.82E-5	1.43E-5
prenol	2.70E-5	3.23E-3	4.33E-3	3.2/E-3	0.8/E-3	8.52E-5	1.13E-4	1.20E-4	1.08E-4	1.31E-5	1.70E-5	2.00E-3
benzaldenyde	5.21E-0	0.32E-0	0.11E-0	0.3/E-0	1.38E-3	1.41E-5	1./1E-3	1.19E-3	1.22E-3	1.2/E-0	1.38E-0	1.35E-0
ouclementsdiane	0.1/E-0	7.91E-0	1.11E-3	1.41E-3	1.92E3	2.41E-0 7.12E-6	3.28E-3	3./1E-3	3.03E-3	3./UE-0	4.80E-0	3./4E-0
cyclopentaulene	1.020-0	2.39E-0	3.01E-0	4./00-0	0.04E-0	1.13E-0	0.435-0	0.010-0	9.83E-0	9.90E-/	1.30E-0	1.035-0
	3.82E-7	3.45E_7	5.58E_7	7.52E-7	1.30E-0	1.026-0	2.17E-0 2.07E-6	2.27E-0	3.00E-0	1.256-7	1.036-/	1720-7
dibenzofuran	2.34E-7	1 09E_7	3.305-7	A 85E_7	7.02E_7	0.91E_7	2.0/E-0	1.77E.6	3.30E-0	1.136-7	1.436-/	2 52 7
nanhthalene	1.20L-7	1.90E-7	5.27L-7	nd	7.02E-7	1.26E_7	2.28E_7	3.51E_7	2.70E-0	2 905-8	1.05E-7	1.02E-7
toluene	nd	nd	nd	1 67E_7	276E_7	3.95E_7	6.45E-7	8 03E-7	137E_6	2.90E=8	4 74E-8	6 02E-8
CO	6.99E-6	9.97E-6	1.51E-5	2.03E-5	2.86E-5	3.68E-5	4 98E-5	5.67E-5	7.95E_5	6.85E_6	9.02E_6	1 14E_5
methane	2.63E-5	3.41E-5	4.79E-5	6.15E-5	8.35E-5	1.06E-4	1.42E-4	1.60E-4	2.15E-4	1.81E-5	2.38E-5	2.88E-5
ethylene	1.75E-7	2.94E-7	5.21E-7	7.14E-7	1.06E-6	1.40E-6	1.96E6	2.46E6	3.28E6	nd	nd	nd
ethane	8.36E-8	1.33E-7	2.39E-7	3.59E-7	6.23E-7	9.37E-7	1.42E-6	1.88E-6	2.89E-6	2.02E-7	3.08E-7	4.10E-7
				Per	centage on	Intake Ani	soled					
anisole	92.08	89.49	85.89	81.39	74.53	66.25	56.91	47.50	35.30	49.14	39.70	30.12
phenol	5.35	6.84	8.95	11.73	15.31	20.52	26.23	32.91	40.40	31.05	36.97	42.16
co	1.38	2.10	3.13	4.52	6.38	8.87	11.59	14.81	19.11	16.22	19.66	24.07
methane	5.21	7.20	9.92	13.70	18.62	25.42	32.92	41.86	51.66	42.88	51.82	60.85
ratio o/p-cresol	1.50	1.44	1.39	1.30	1.22	1.14	1.05	0.99	0.85	1.09	1.15	1.22

<sup>a</sup> Concentrations given at 1.0 atm and the applied reaction temperature. For the experiments a tubular reactor was used (5.25 mL). <sup>b</sup> Flows in mmol/h: high-concentration range, 2.0–2.4 mmol/h anisole, 28.1 mmol/h hydrogen, 42.3 mmol/h nitrogen; last 3 temperatures, 0.2–0.23 mmol/h anisole, 28.4 mmol/h hydrogen, 39.1 mmol/h nitrogen. O-balance of products always larger than 99%. <sup>c</sup> Not detected (nd) products are below integration level (1E–9 M). <sup>d</sup> Percentages corrected to O-balance being 100%. <sup>e</sup> Where 5.05E-4 is  $5.05 \times 10^{-4}$ .

TABLE IV:	Hvdrogenolvsis	of Anisole in	High-Temperature Region <sup>*</sup>
	11,010E6001,010	AT LTINGALA IN	THEN I CHIPCIGUMIC INCEICH

			<u> </u>							
temp (K)	983	993	998	1003	1007	1010	1013	1015	1018	1020
residence time (s)	0.0165	0.0163	0.0151	0.0151	0.0156	0.0162	0.0162	0.0161	0.0167	0.0173
pressure (atm)	1.2	1.2	1.2	1.2	1.25	1.3	1.3	1.3	1.35	1.4
				Inflow (	M) <sup>b</sup>					
anisole	3.97E-4d	3.75E-4	2.00E-4	1.78E-4	1.92E-4	1.88E-4	1.91E-4	1.86E-4	1.94E4	2.00E-4
hydrogen	6.52E-3	6.46E-3	6.51E-3	6.49E3	6.73E-3	6.98E3	6.96E-3	6.95E-3	7.19E-3	7.44E-3
nitrogen	7.96E-3	7.89E-3	7.94E3	7.92E-3	8.21E-3	8.52E-3	8.49E-3	8.48E-3	8.78E-3	9.08E-3
•				Outflow	(M)					
anisole	3.09E-4	2.80E-4	1.23E-4	1.01E-4	1.01E-4	9.55E-5	9.13E-5	8.66E-5	8.07E-5	7.63E-5
phenol	4.67E-5	5.13E-5	4.43E-5	4.36E-5	5.12E-5	5.20E-5	5.62E-5	5 64E-5	6 38E-5	6.98E-5
benzaldehvde	6.55E-6	6.97E-6	4.66E-6	4.37E-6	4.88E-6	4.84E-6	5.10E-6	5.41E-6	5.38E-6	5 68E-6
benzene	8.83E-6	9.56E-6	7.61E-6	7.50E-6	8.92E-6	9.12E-6	9.77E_6	9.07E-6	1 13E-5	1.25E_5
cvclopentadiene	5.08E-6	6.14E-6	7.32E-6	6.81E-6	9.01E-6	9.34E-6	1.02E-5	1.02E-5	1.21E-5	1.36E-5
methylcyclopentadiene	nd	2.87E-6	2.04E-6	3.41E-6	2.76E-6	2.89E-6	3.15E-6	3.18E-6	3.57E-6	3.80E-6
o-cresol	8.25E-6	9.55E-6	4.17E-6	3.95E-6	4.58E-6	4.59E-6	4.73E-6	4.68E-6	4.78E-6	4.78E-6
p-cresol	6.97E-6	6.58E-6	3.11E-6	2.74E-6	3.43E6	3.40E-6	3.55E-6	3.52E-6	3.66E-6	3.71E-6
dibenzofuran	5.82E-7	6.47E-7	4.76E-7	4.22E-7	5.91E-7	5.73E-7	6.60E-7	6.69E-7	7.96E-7	8.66E-7
2.2'-dihydroxybiphenyl	nd	nd	8.34E-8	7.77E-8	8.48E-8	1.15E-7	1.18E-7	8.91E-8	1.22E-7	1.23E-7
naphthalene	nd	nd	7.93E-8	9.88E-8	8.22E-8	8.41E-8	8.96E-8	8.90E-8	9.27E8	9.28E-8
1-methylnaphthalene	nd	nd	2.58E-7	5.31E-7	3.66E-7	3.90E-7	4.47E-7	4.48E-7	5.52E-7	6.37E-7
toluene	nd	2.10E-7	9.98E-8	1.11E-7	1.44E-7	1.58E-7	1.76E-7	1.81E-7	2.22E-7	2.55E-7
СО	1.58E5	1.97E-5	1.99E-5	2.05E-5	2.52E-5	2.62E-5	2.87E-5	2.91E-5	3.43E-5	3.89E-5
methane	5.00E-5	5.71E-5	5.85E-5	5.83E-5	6.94E-5	7.17E-5	7.72E-5	7.73E-5	8.97E-5	9.99E-5
ethylene	3.33E-7	3.88E-7	3.40E-7	3.91E-7	5.70E-7	6.15E-7	7.15E-7	7.28E-7	8.98E-7	1.04E-6
ethane	1.21 <b>E6</b>	1.58E-6	4.95E-7	5.39E-7	6.61E-7	7.11E-7	7.43E-7	7.75E-7	8.41E-7	8.71E-7
			Perc	entage on In	take Anisole	c				
anisole	77.86	74.49	61.31	56.85	52.62	50.83	47.81	46.50	41.66	38.19
phenol	11.76	13.68	22.16	24.52	26.76	27.69	29.43	30.26	32.92	34.96
co	3.98	5.25	9.94	11.52	13.16	13.94	15.03	15.60	17.72	19.45
methane	12.59	15.22	29.24	32.76	36.24	38.16	40.43	41.50	46.27	50.02

<sup>a</sup> Concentrations are consistent with applied reaction pressure and temperature. Tubular quartz reactor of 30.8E-6 L used. <sup>b</sup> Flows in mmol/h: 1.3–2.8 mmol/h anisole, 46.7 mmol/h hydrogen, 57.0 mmol/h nitrogen. O-balance of products always >99%. <sup>c</sup> Percentages are corrected for total O-containing products being 100%. <sup>d</sup> Where 3.97E-4 is  $3.97 \times 10^{-4}$ .

organic oxygen. The organic O-balance—CO included—is always better than 99%, meaning that reaction 6 will be of limited importance.

Cresol (o + p) results from the cross combination of methyl and phenoxyl radicals (reaction 4). An amount of 1-2% (on anisole intake) is formed in the lower temperature range and 4-5% in the higher temperature range (Tables III and IV). The detection of cresols as products implies the back-formation of anisole; however this will always be less than 0.5% (on anisole intake), taking into account the spin distribution in the phenoxyl radical (9% on "O").<sup>26</sup> In a separate study on the rate of recombination of phenoxyl and CH<sub>3</sub> in the temperature range of 450–750 K (reaction 4 and the reverse of reaction 1), a temperature independent product ratio of anisole/o-cresol/p-

### Thermolysis of Anisole in a Hydrogen Atmosphere

cresol = 0.25:1.53:1.00 was observed. The o/p ratio is consonant with parameters advanced for the spin density distribution in the phenoxyl radical.

The presence of methylcyclopentadiene<sup>27</sup> in the higher temperature range (see Table IV) suggests that cresols eliminate CO similar to reaction 3. Alternatively, methylcyclopentadiene may arise by recombination of methyl and cyclopentadienyl. In section 3 we will discuss this point further and explain that another mode of formation is more important.

The foregoing indicates that cresols are not stable in this system; moreover, the o/p cresol ratio changes with temperature, from o/p = 1.50 (793 K) to o/p = 0.85 (873 K). This could be the result of selective degradation of the ortho isomer. Therefore separate experiments were performed with a 1:1 mixture of oand p-cresol at 873 and 913 K together with hexamethylethane—a source of H-atoms<sup>28</sup>—in a nitrogen atmosphere, residence time 2.5 s. The resulting o-/p-cresol ratio was 0.94 (873 K, total conversion of cresols 12.3%) and 0.93 (913 K, total conversion of cresols 19%). Thus the o/p ratio is not much effected, meaning that the thermal decomposition of the cresols is about equally important. Lin<sup>29</sup> determined branching ratios for the collision complexes of methyl and phenoxyl, toward isomerization (to give cresols directly) or stabilization to give the keto form of the cresols, near atmospheric pressures. At 823 K, isomerization, which process will be nonselective for the ortho or para isomer, is about 10 times faster.

Apparently with increasing temperature, the difference in rate of enolization of the o- and p-keto form becomes important, resulting in a decrease of the ortho isomer in the product mixture.

In the higher temperature region the ratio of CO to the sum of cyclopentadiene and methylcyclopentadiene is ca. 2. If CO is the result of reaction 3 and if all (methyl) cyclopentadienyl radicals end up as the parent hydrocarbon, this ratio should be unity. However,  $(CH_3)C_5H_4$  may well in part form benzene<sup>27</sup> or polycyclic aromatics. In the lower temperature region (where methylcyclopentadiene is not observed) the  $CO/C_5H_6$  product ratio is 4–8, which strongly points at additional mechanisms for CO formation. We will argue later on that this additional CO stems from the induced decomposition of anisole. At this point it is appropriate to discuss the radical induced decomposition of anisole for which atomic hydrogen—produced in reaction 15—is the most likely candidate. Reactions 17 and 18 can be envisaged.

$$PhOCH_3 + H^{\bullet} \rightarrow PhH + CH_3O^{\bullet}$$
(17)

$$PhOCH_3 + H^{\bullet} \rightarrow PhOCH_2^{\bullet} + H_2$$
(18)

Reaction 17 is analogous to hydrodesubstitution in the case of phenol and other monosubstituted benzenes.<sup>16</sup> CH<sub>3</sub>O<sup>•</sup> will loose H because H-abstraction or isomerization to <sup>•</sup>CH<sub>2</sub>OH will be slow under these conditions.<sup>30</sup> However the resulting formal-dehyde could not be analyzed in our system. In view of the O-balance (>99%), formaldehyde, if formed, must have been decomposed into CO and H<sub>2</sub>. Reaction 18 is analogous to hydrogen attack at dimethyl ether.<sup>31</sup> The anisyl radical, as shown in Scheme II, will undergo an 1,2 aryl shift to give the benzyloxy radical, and the subsequent loss of H results in benzaldehyde.<sup>23,32</sup>

Benzaldehyde itself is partially converted under our conditions to CO and phenyl radicals (reaction 21). The CO formed from both reactions should be accompanied by an equimolar amount of benzene. In Figure 5, the yields of benzene and CO are compared and the difference in the low-temperature regime is a factor 2, increasing to 3 at the higher temperatures, meaning that 30-50% of the CO is accounted for by reactions 17 and 21. When the yield of CO is corrected by subtracting the amount of benzene and compared with the yield of "cyclopentadiene moieties",<sup>33</sup> as done in Figure 6, we see that at low conversions of anisole it matches quite well, which tallies with the proposed mechanism. At high conversions, however, the yield of cyclopentadiene is too



Figure 5. Anisole pyrolysis in a hydrogen atmosphere: yields of CO and benzene (expressed as mole percent of initial anisole intake) as a function of temperature. Low-temperature region,  $t_{res} = 3.8$  s; high-temperature region,  $t_{res} = 0.012$  s.



Figure 6. Anisole pyrolysis in a hydrogen atmosphere: yields of cyclopentadienyl derivatives (Cp) compared with CO production resulting from decomposition of phenoxyl or phenol (expressed as mole percent of initial anisole intake) as a function of temperature. Low-temperature region,  $t_{\rm res} = 3.8$  s; high-temperature region,  $t_{\rm res} = 0.012$  s. Symbols:  $(\blacksquare, \blacklozenge)$  assumed equal to CO-benzene, see text;  $(+, \blacktriangle)$  yield of cyclopentadiene + methylcyclopentadiene + methyl-naphthalene.

# SCHEME II: Formation of Benzaldehyde and Benzene from Anisole

BENZALDEHYDE FORMATION



low, which probably is due to the previously mentioned loss of cyclopentadienyl radicals giving polycyclic aromatics. A remarkably high yield of ethylene is observed which might be coupled to cyclopentadienyl degradation.<sup>16</sup>

In sum, the hydrogenolysis of anisole is a rather complex phenomenon involving primary O-C homolysis, induced decomposition, and numerous additional steps, leading to a variety of products. In order to better understand the reaction profiles, including product yields as a function of temperature, reaction modeling is the instrument of choice.

		log A	<i>T</i> **	Ea	ref	k(823K) (M <sup>-1</sup> s <sup>-1</sup> , s <sup>-1</sup> )
T-1 (1)	$PhOCH_3 \rightarrow PhO^{\circ} + CH_3^{\circ}$	15.3		63.6	Ь	$2.52 \times 10^{-2}$
T-2 (13)	$PhO^{\bullet} + H_2 \rightarrow PhOH + H^{\bullet}$	9.96		26.6	16	$7.80 \times 10^{2}$
T-3	$PhO^{\bullet} + PhOCH_{3} \rightarrow PhOH + PhOCH_{2}^{\bullet}$	8.62		16.06	c	$2.25 \times 10^{4}$
T-4 (3)	$PhO' \rightarrow CO + Cp'$	11.4		43.9	12	$5.51 \times 10^{-1}$
T-5 (15)	$CH_{1} + H_{2} \rightarrow CH_{4} + H^{*}$	3.62	1.83	10.48	d	$1.49 \times 10^{6}$
( /		-0.18	3.0	7.74	d	
T-6 (12)	$CH_3$ + PhOCH <sub>3</sub> $\rightarrow$ $CH_4$ + PhOCH <sub>2</sub> .	8.7		10.5	32	8.13 × 10 <sup>5</sup>
T-7 (5)	$2CH_3^* \rightarrow C_2H_6$	13.96	-1.18	0.65	36	$2.22 \times 10^{10}$
T-8 (4)	$CH_3^{\bullet} + PhO^{\bullet} \rightarrow o/p$ -cresole	10.15			е	$1.40 \times 10^{10}$
T-9	$CH_3$ + PhO $\rightarrow$ PhOCH <sub>3</sub>	9.1			f	$1.40 \times 10^{9}$
T-10(16)	2PhO <sup>•</sup> → dibenzofuran + H <sub>2</sub> O	8.7			g	$5.01 \times 10^{8}$
T-11 (14)	$PhO^{\bullet} + H^{\bullet} \rightarrow PhOH$	11.8-13			ĥ	$1.00 \times 10^{13}$
T-12 (23)	$H^{\bullet} + PhOCH_3 \rightarrow PhOH + CH_3^{\bullet}$	9.85		5.39	i	$2.62 \times 10^{8}$
T-13 (18)	$H^{\bullet} + PhOCH_3 \rightarrow PhOCH_3^{\bullet} + H_2$	9.12		3.89	31	$1.22 \times 10^{8}$
T-14 (20)	$PhOCH_{2}^{\bullet} \rightarrow PhCOH + H^{\bullet}$	12.5		21.5	23	$6.13 \times 10^{6}$
T-15 (17)	$H^{\bullet} + PhOCH_{1} \rightarrow PhH + CO + H_{2} + H^{\bullet}$	9.55		5.39	8	$1.33 \times 10^{8}$
T-16	$H^{\bullet} + CH_{4} \rightarrow H_{2} + CH_{3}^{\bullet}$	1.35	3	8.76	37	$5.87 \times 10^{7}$
T-17 (7)	$H^{\bullet} + PhOH \rightarrow H_{2} + PhO^{\bullet}$	10.2		6.1	16	$3.79 \times 10^{8}$
T-18 (6)	$H^{\bullet} + PhOH \rightarrow OH + PhH$	9.85		5.39	16	$2.62 \times 10^{8}$
T-19 (24)	$H^{\bullet} + PhOH \rightarrow CO + C_{4}H_{7}^{\bullet}$	10.4		4.7	h	$1.42 \times 10^{9}$
T-20	$H^{\bullet} + CH_{3}$ -Ph-OH $\rightarrow$ PhOH + CH <sub>3</sub> .	10.08		5.12	28b	$5.24 \times 10^{8}$
T-21	$H^{\bullet} + CH_{2} - Ph - OH \rightarrow Ph CH_{2} + {}^{\bullet}OH$	9.85		5.39	16	$2.62 \times 10^{8}$
T-22	$H^{\bullet} + CH_{3}$ -Ph-OH $\rightarrow H_{2} + {}^{\bullet}CH_{2}$ -Ph-OH	-7.12	5.5	0.34	38	$6.70 \times 10^{8}$
T-23	$H^{\bullet} + CH_{2} - Ph - OH \rightarrow H_{2} + CH_{2} - Ph - O^{\bullet}$	10.2		6.1	16	$3.79 \times 10^{8}$
T-24	$H^{\bullet} + {}^{\bullet}CH_{2}$ -Ph-OH $\rightarrow CH_{3}$ -Ph-OH	11.3		•	est	$2.00 \times 10^{11}$
T-25	H <sup>•</sup> + CH <sub>2</sub> -Ph-O <sup>•</sup> → CH <sub>2</sub> -Ph-OH	11.3			est	$2.00 \times 10^{11}$
T-26	$H^{\bullet} + CH_{2} - Ph - OH \rightarrow CO + C_{6}H_{6} + H_{2} + H^{\bullet}$	10.4		4.7	i	$1.42 \times 10^{9}$
T-27	$CH_3$ -Ph-O <sup>•</sup> $\rightarrow CO + C_6H_6 + H^•$	11.4		43.9	k	$5.51 \times 10^{-1}$
T-28	$H^{\bullet} + CH_{3}^{\bullet} \rightarrow CH_{4}$	12.08	0.4		37	$8.19 \times 10^{10}$
T-29	$H^{\bullet} + Cp^{\bullet} \rightarrow CpH$	11.3			est	$2.00 \times 10^{11}$
T-30	$CH_3^{\bullet} + Cp^{\bullet} \rightarrow CpCH_3$	9.1			est	$1.40 \times 10^{9}$
T-31	$2Cp^{\bullet} \rightarrow naphthalene$	8.0			est	$1.00 \times 10^{8}$
T-32	$C_4H_7^* \rightarrow C_0H + H^*$	15.5		32	est	$1.00 \times 10^{7}$
T-33 (25)	$C_1H_2 \rightarrow C_2H_4 + C_2H_2$	15.5		35.5	ī	$1.18 \times 10^{6}$
T-34	$Ph^{\bullet} + H_{2} \rightarrow PhH + H^{\bullet}$	1.48	2.63	8.54	m	7.57 × 10 <sup>6</sup>
T-35	$OH + H_2 \rightarrow H_2O + H_2$	5.0	1.6	3.30	34	$6.15 \times 10^{8}$
T-36 (21)	$H^{\bullet} + PhCOH \rightarrow H_{2} + Ph^{\bullet} + CO$	10.6		4.21	n	$3.03 \times 10^{9}$
T-37	$2C_{1}H_{1} \rightarrow PhH$	8.0			est	$1.00 \times 10^{8}$

TABLE V: Rate Expressions Used in Modeling Thermolysis of Anisole in a Hydrogen Atmosphere\*

<sup>a</sup> In units of s<sup>-1</sup> and M<sup>-1</sup> s<sup>-1</sup>. Numbers between brackets refer to the reaction numbers used in the text. <sup>b</sup> This work. <sup>c</sup> H<sup>•</sup>-transfer to and from a resonance stabilized radical; see ref 24. <sup>d</sup> For the lower temperature region the value of Schatz<sup>35</sup> was used, whereas in the high-temperature region the (higher) value of Warnatz<sup>24</sup> was used. <sup>e</sup> Stated equal to benzyl + CH<sub>3</sub><sup>•</sup>.<sup>15 /</sup> Stated equal to 0.10 times the formation of cresols, according to spin densities (see text). <sup>e</sup> Fitted to data. T-10 is the overall result of reaction 16 as given in text. A hydrogen atom abstracts H from 2,2'-dihydroxybiphenyl, and by subsequent OH<sup>•</sup> release another H<sup>•</sup> is formed together with benzofuran, so no chain branching occurs. The estimated rate constant is close to the one in ref 26 ( $k_{16} = 10^{8.2}$  M<sup>-1</sup> s<sup>-1</sup>). <sup>b</sup> See text. <sup>i</sup> See text, rate constant as for addition of H<sup>•</sup> at ipso-position in phenol. <sup>j</sup> As for phenol, see text; formed methyleyclopentadiene ends up as benzene. <sup>k</sup> As for phenoxyl, ref 12. <sup>j</sup> See text, rate constant fitted to ratio cyclopentadiene/ethylene. <sup>m</sup> As for vinyl radical, ref 37. <sup>n</sup> As for acetaldehyde, ref 37.

3. Reaction Modeling. A model consisting of 37 reactions and 23 species is outlined in Table V.<sup>34–38</sup> With the use of the program KINAL and with substitution of the initial concentrations and residence times at a chosen temperature, the final concentrations of each species can be calculated. Kinetics were based on thermally equilibrated adduct radicals.<sup>39</sup>

The results for the 793-873 K region are collected in Table VI.

The given reactions account for most of the products in that temperature region. In Figures 7 and 8 pertinent calculated and observed product profiles are shown as a function of temperature. Only a small number of back-reactions is incorporated; in general their contribution is negligible. This is reasoned in Appendix C.

To reproduce the temperature dependence of the anisole conversion in conjunction with the formation of especially benzene and CO, it proved to be necessary to introduce a reaction of anisole with H to yield phenol and methane, reaction 23. Without

$$H^{\bullet} + PhOCH_3 \rightarrow PhOH + CH_3^{\bullet}$$
 (23)

this reaction, the calculated degree of conversion of anisole was much more temperature dependent, with a rate being too low at lower temperatures. Increasing the rate for reactions 17 and 18, resulted in too high yields of benzene and CO. Therefore induced decomposition leading to phenol appears to take place. A possible mechanism for reaction 23 is addition to H<sup>\*</sup> to the ortho- or



Figure 7. Modeling of anisole conversion in a hydrogen atmosphere: Lines represent model calculations whereas dots are measured yields. Yields of anisole, phenol, and methane are expressed in mole percent of anisole intake.

para-position of the aromatic nucleus, followed by methyl elimination, resulting in o- and p-ketophenol (exemplified in Scheme III and Figure 9). These intermediates, for the major part, ultimately yield phenol (vide infra). A less likely possibility is attack of H at the oxygen atom of anisole to give phenol directly. The overall rate constant for reaction 23 was taken equal to that for H-addition to the ipso position in phenol.

A problem is to account for the right amount of CO, partially

### **TABLE VI: Modeling All Temperatures**

For Conditions Outlined in Table III									
temp (K)	793	803	813	823	833	843	853	863	873
			Inta	ike Anisol (N	<b>A</b> )				
	5.05E-4ª	4.74E-4	4.83E-4	4.49E4	4.49E-4	4.15E-4	4.30E-4	3.83E-4	4.16E-4
			Calcula	ted Outflow	s (M)				
anisole	4.67E-4	4.27E-4	4.20E-4	3.71E-4	3.45E-4	2.88E-4	2.58E-4	1.87E-4	1.50E-4
phenol	2.13E-5	2.70E-5	3.72E5	4.68E5	6.28E-5	7.75E-5	1.04E-4	1.20E-4	1.57 <b>E-4</b>
benzaldehyde	6.52E-6	7.10E-6	8.49E6	8.94E6	1.02E-5	1.01E-5	1.15E-5	1.03E-5	1.15E-5
benzene	7.85E-6	9.20E-6	1.19E-5	1.35E-5	1.67E-5	1.85E-5	2.35E-5	2.43E-5	3.15E-5
cyclopentadiene	1.37E-6	2.06E-6	3.42E-6	4.98E6	7.80E-6	1.09E-5	1.69E-5	2.14E-5	3.21E-5
o-/p-cresole	3.78E-7	5.77E-7	1.01E6	1.51E6	2.48E-6	3.56E-6	5.85E-6	7.26E-6	1.16E-5
dibenzofuran	1.79E-7	3.05E-7	5.72E-7	9.32E-7	1.63E-6	2.50E6	4.28E-6	5.75E-6	9.40E-6
toluene	4.18E-9	7.61E-9	1.61E8	2.81E8	5.45E-8	9.00E-8	1.74E-7	2.44E-7	4.59E-7
methylcyclopentadiene	1.19E-9	2.27E-9	4.78E-9	8.90E-9	1.77E-8	3.16E-8	6.24E8	9.77E-8	1.84E7
naphthalene	3.48E-11	8.76E-11	2.26E-10	5.44E-10	1.32E-9	3.00E-9	6.99E-9	1.46E-8	3.22E-8
co	9.03E-6	1.10E-5	1.48E-5	1.78E-5	2.33E-5	2.79E-5	3.80E-5	4.27E-5	5.92E-5
methane	2.33E-5	3.01E-5	4.26E-5	3.49E-3	7.57E-5	9.61E-5	1.34E-4	1.58E-4	2.16E-4
ethane	6.81E-8	9.52E-8	1.60E-7	2.25E-7	3.62E-7	5.04E-7	8.40E-/	1.03E-6	1./SE-0
ethylene	1.48E-7	2.30E-7	3.8/E-/	5.79E-7	9.32E-/	1.34E-6	2.12E-0	2.75E-6	4.21E-0
H <sub>2</sub> O	4.58E-7	/.29E-/	1.28E-6	1.98E-6	3.29E-6	4.85E-6	/.99E0	1.05E5	1.0/E-3
phenoxyl	1.196-8	1.555-8	2.12E-8	2.09E8	3.52E-8	4.29E-8	2.43E-8	0.00E-0	/.20E-8
H-atom	2.09E-11	2.41E-11	2./SE-11	3.0/E-11	3.42E-11	3.00E-11	3.93E-11	3.92E-11	3.916-11
metnyi	0.93E-10	8.30E-10	1.10E-9	1.31E-9	1.002-9	1.916-9	2.30E-9	2.385-9	2.0/E-9
cyclopentadienyl	4.45E-10	7.00E-10	1.13E-9	1./3E-9	2./2E-9	4.085-9	0.18E-9	0.0/E-9	1.3UE-0
	J.12E-14	4.365-14	/.34E-14	1.0/E~13	1.03E-13	2.19E-13	) 3.24E-13	3.//E-13	5.06E-13
pnenyi	1.0/2-11	1.206-11	1.06E-11	1.0/E-11	2.25E-11	2.306-11	2.09E-11	2.296-11	2.4/6-11
			For Conditio	ns Outlined	in Table IV	, 	<u>.</u>		
temp (K)	998	1003	1007	1010	1	.013	1015	1018	1020
			Inta	ike Anisol (N	()				
	2.00E-4	1.78E-4	1.92E-4	1.881	3-4 1	.91E-4	1.86E4	1.94E4	2.00E-4
			Calcula	uted Outflow	s (M)				
anisole	1.25E-4	1.04E4	1.04E-4	9.401	3-5 9	0.02E5	8.48E-5	8.02E-5	7.63E-5
phenol	4.47E-5	4.43E-5	5.21E-5	5.511	3-5 5	.86E-5	5.89E-5	6.52E-5	7.00E-5
benzaldehvde	3.29E6	2.92E-6	3.22E-6	3.19	E6 3	.23E-6	3.11E6	3.26E6	3.37E6
benzene	9.62E6	9.03E6	1.08E-5	5 1.14	E-5 1	.20E-5	1.28E-5	1.35E-5	1.49E-5
cvclopentadiene	6.31E6	6.49E6	8.36E-6	i 9.411	E6 1	.04E5	1.06E-5	1.26E-5	1.43E-5
$o_{-} + p_{-}$ cresol	4.32E6	4.15E6	5.14E6	5.331	E6 5	5.90E6	5.93E6	6.66E6	7.12E-6
dibenzofuran	2.69E6	2.69E6	3.48E6	i 3.83]	E6 4	.27E6	4.33E-6	5.12E-6	5.75E-6
toluene	1.16 <b>E</b> -7	1.15E-7	1.58E7	1.761	37 2	2.03E-7	2.06E-7	2.52E-7	2.88E-7
methylcyclopentadiene	1.92E8	2.04E8	2.72E-8	3.031	E8 3	.53E-8	3.67E8	4.41E-8	4.95E-8
naphthalene	8.23E-10	1.01E-9	1.46E-9	1.82	E-9 2	2.23E9	2.43E-9	3.21E-9	3.91E-9
CÔ	1.51E-5	1.47E5	1.81E-5	5 1. <b>96</b> 1	E—5 2	2.11E-5	2.12E-5	2.45E-5	2.73E-5
methane	5.82E-5	5.81E5	6.98E-5	5 7.501	E-5 8	3.05E5	8.12E-5	9.17E-5	1.00E-4
ethane	6.08E-7	5.69E7	7.03E7	7.14	3–7 8	6.01E-7	8.01E-7	8.99E-7	9.50E-7
ethylene	9.96E7	1.03E6	1.33E-6	5 1.511	E6 1	67E6	1.69 <b>E6</b>	2.03E6	2.31E-6
H <sub>2</sub> Ò	4.16E6	4.20E6	5.43E-6	6.031	E6 6	5.70E6	6.80E–6	8.07 <b>E6</b>	9.12E-6
phenoxyl	6.54E7	6.47E7	7.10E-7	7.191	37 7	′.48E–7	7.50E-7	7.82E7	7. <b>99E-7</b>
H-atom	5.58E-9	5.54E9	5.65E9	5.58	E-9 5	5.61 <b>E9</b>	5.60E-9	5.54E-9	5.46E9
methyl	3.41E8	3.21E8	3.38E8	3.21	E—8 3	3.30 <b>E</b> 8	3.26E8	3.21E-8	3.11E-8
cyclopentadienyl	3.32E8	3.69E8	4.34E8	4.76	E8 5	5.25E8	5.50E8	6.19E8	6.70E-8
OH	1.65E11	1.63E-11	l 1.87E–1	1 1.881	3-11 2	2.03E-11	2.03E-11	2.15E-11	2.20E-11
phenyl	4.30E-10	3.72E-10	) 3.96E–1	.0 3.68]	E-10 3	i.70E–10	3.53E-10	3.49E10	3.41E-10

<sup>a</sup> Where 5.05E-4 is  $5.05 \times 10^{-4}$ .

accompanied by cyclopentadiene as outlined previously (70–50% of total CO, depending on temperature) and without producing benzene. If decomposition of phenoxyl would have to cover this CO, its rate must be taken considerably (at least 100 times) larger than the currently accepted value<sup>12</sup> based on  $k_3 = 10^{11.4} \exp[(-43.9 \text{ kcal mol}^{-1})/RT]$ . Therefore an additional CO forming reaction was introduced:

$$H^{\bullet} + PhOH \rightarrow CO + C_{s}H_{7}^{\bullet}$$
 (24)

Recalling that phenol formed via reactions 14 and 23—in the first instance—is the keto tautomer (see Discussion), the mechanism as depicted in Scheme IV is proposed. The energy diagram (Figure 10) shows that the first step is rate determining and that breaking of the C–C-bond in the keto intermediate A is 13 kcal/ mol endothermic.  $k_{24}$  was estimated as  $10^{10.4} \exp[(-4.7 \text{ kcal mol}^{-1})/\text{RT}]$ , four times the value for an unsubstituted ring position in phenol.<sup>6</sup> The reason why this reaction has not been found earlier for instance in the hydrogenolysis of phenol<sup>16</sup> must be the relatively high concentrations of H<sup>•</sup> and ketophenol combined



Figure 8. Modeling of anisole conversion in a hydrogen atmosphere: lines represent model calculations whereas dots are measured yields. Yields of methane, benzene, and cyclopentadiene are expressed in mole percent on anisole intake.



---> R.C.

Figure 9. Energy diagram for  $H^{\bullet}$  + PhOCH<sub>3</sub>  $\rightarrow$  PhOH + CH<sub>3</sub><sup>•</sup>. Heats of formation estimated with group additivity rules. See also text and Appendix I.



--> R.C.

Figure 10. Energy diagram for reaction 24 as outlined in Scheme IV. Heats of formation estimated with group additivity rules.

## SCHEME III: Formation of Phenol from Anisole by Attack of H<sup>•</sup>



SCHEME IV: Possible Mechanism for Reaction 24; Formation of CO and 3-Cyclopentenyl by Attack of H<sup>•</sup> at the Meta Position of o-Ketophenol



with the low temperature. Analogous reactions involving o-/ p-ketocresol—formed via recombination of PhO• and CH<sub>3</sub>• (reaction 4)—can give rise to methylcyclopentenyl and CO. Methylcyclopentenyls are likely to end up as benzene.

The cyclopentenyl radical formed in reaction 24 will eliminate  $H^{\bullet}$  (activation energy of 32 kcal/mol) rather than recombine with  $H^{\bullet}$  or react with hydrogen. As to ethylene, direct formation of ethylene from ethane, through H-abstraction to give the ethyl radical followed by loss of H, is too slow according to known kinetic data.<sup>30</sup> Even with a calculated H-atom concentration of

TABLE VII: Routes to Benzene

			ben	% of tota zene for	l med
_		reaction	793 K	823 K	873 K
1	T-15	ipso substitution of anisole	69	54	18
2	T-36	conversion of PhCOH	23	30	29
3	T-18	conversion of phenol	6.4	13	35
4	T-26	conversion of cresol by attack of H <sup>•</sup>	0.6	2.4	14
5	<b>T-27</b>	rearrangement of methylphenoxyl	0.06	0.4	4.0

 $3 \times 10^{-11}$  M, this would only account for 0.2% of the ethylene observed. We believe its origin could be coupled to a C5-intermediate, because ethylene was also observed in phenol pyrolysis,<sup>16</sup> and, in our model, decomposition of cyclopentenyl was *modeled* to give the right amount of ethylene. A sound thermokinetic rationale for ethylene formation, however, cannot be given.

With our model, it is possible to quantify the importance of the different routes leading to, e.g., benzene, as depicted in Table VII. Interestingly H-attack on (keto)cresol to give methylcyclopentenyl as an intermediate accounts still for a sizeable part of the benzene formation at high temperatures (14% at 873 K).

As to reaction 14 (recombination of PhO<sup>•</sup> + H<sup>•</sup> to give phenol) Tsang<sup>28a</sup> determined a rate constant of  $2 \times 10^{11}$  M<sup>-1</sup> s<sup>-1</sup>. In our model we have artificially increased this rate (50 times), accepting PhO<sup>•</sup> as the sink for H<sup>•</sup> atoms. Leaving out this acceleration leads to an extremely high calculated phenoxyl concentration (accompanied by unrealistic yields of cresol and dibenzofuran) and also increases the H<sup>•</sup> concentration (leading to twice as much induced decomposition, and therefore to a higher degree of the overall anisole conversion). Such a high effective rate of recombination of phenoxyl and H cannot hold for a simple bimolecular gas-phase process, but recombination of these species could possibly be accelerated at the reactor wall.<sup>40</sup>

The cresols formed in our system are not stable. At 823 K their conversion amounts to 16% and to 27% at 873 K. Abstraction of a H-atom from the methyl or hydroxyl group of cresol yields the substituted benzyl and phenoxyl radicals, respectively. Both species are likely to revert to substrate, decomposition of methylphenoxyl to give CO being insignificant (cf. behavior of phenoxyl). The calculated toluene yield appears to be too low by a factor 3 at 873 K. The rate constant used for desubstitution of cresol to produce toluene-reaction T-21 (Table V)-is taken equal to that for the dehydroxylation of phenol. The recombination of phenyl and methyl cannot account for this difference; with [Ph<sup>•</sup>] =  $2.5 \times 10^{-11}$  M and [CH<sub>3</sub><sup>•</sup>] =  $2.7 \times 10^{-9}$  M and taking a recombination rate constant of  $1.4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  (873 K), this would result in an additional yield of toluene of  $3 \times 10^{-9}$ M, meaning a contribution of 2% only. Another route is the addition/elimination of  $CH_3$  + PhOCH<sub>3</sub> to form PhCH<sub>3</sub> +  $CH_3O^{\bullet}$ , which is overall endothermic by 2 kcal/mol. Rate parameters for this reaction are not known. If this process would account for this difference, then a rate constant of  $6.4 \times 10^5 \, M^{-1}$  $s^{-1}$  can be derived at 873 K (with [CH<sub>3</sub>\*] = 2.7 × 10<sup>-9</sup> and  $[PhOCH_3] = 1.5 \times 10^{-4} \text{ M}$  from Table VI). It must be emphasized that this route will not noticeably change the conversion of anisole.

Although the mechanism still is not very well defined, formation of dibenzofuran is thought to involve the recombination of two phenoxyl radicals,<sup>25</sup> with an overall rate constant of  $10^{8.7}$  M<sup>-1</sup> s<sup>-1</sup>. Dibenzofuran production reflects the phenoxyl radical concentration in the reactor. It has been calculated at a perceptive level from ca. 793 K on, in agreement with the data in Table III, but increases somewhat too rapidly compared to the experimental values. At 863 K the model predicts three times the observed amount.

4. Principal Component Analysis. According to the method described by Turanyi et al.,<sup>19</sup> a principal component analysis was carried out: The kinetic information inherent in the relative reaction rate matrix is extracted. Eigenvalue-eigenvector de-

 
 TABLE VIII:
 Eigenvalues and Eigenvector Elements from the Analysis of Anisole Decomposition at 3.77 s at 823 K

no.	eigenvalue	significant (>0.1) eigenvector elements <sup><math>a,b</math></sup>
1	1.4E+11°	T-5 (0.77), T-1 (-0.61), T-12 (0.20)
2	3.8E+9	T-11 ( $-0.69$ ), T-5 (0.49), T-19 ( $-0.22$ ), T-32 (0.19), T-14 (0.17), T-15 (0.12), T-13 (0.12)
3	8.4E+8	T-19 (0.71), $T-32$ (-0.64), $T-11$ (-0.21), $T-1$ (0.14),
4	4.4E+8	T-36 (-0.70), T-34 (0.70)
5	6.9E+7	T-14 (0.79), T-13 (0.55), T-6 (-0.16), T-1 (0.16)
6	3.6E+7	T-35 (–0.72), T-18 (0.70)
7	2.5E+6	T-15 (0.72), T-17 (0.52), T-10 (0.35), T-3 (0.22), T-2 (0.12), T-33 (-0.10)

<sup>a</sup> Figures before the brackets refer to the numbering as indicated in Table V, while the eigenvector elements are given in brackets. <sup>b</sup> Reactions which can be eliminated, according to principal component analysis are T-16 and T-28. <sup>c</sup> Where 1.4E+11 is  $1.4 \times 10^{11}$ .



Figure 11. Modeling of anisole conversion in a hydrogen atmosphere in the 983-1020 K temperature region ( $t_{res} = 0.012$  s): lines represent model calculations whereas dots are measured yields. Yields of anisole, phenol, and CO are expressed in mole percent on anisole intake.

composition of the cross-product matrix  $\mathbf{F}$  has been performed at several time intervals at 823 K. Listed in Table VIII, as an example, are the largest eigenvalues together with the significant elements of the corresponding eigenvectors for a reaction time of 3.77 s.

It can be seen that the first principal components, 1-7, identify the major formation and consumption reactions of the highly reactive species (radicals) in our system. These are respectively, CH<sub>3</sub><sup>•</sup>, H<sup>•</sup>, C<sub>5</sub>H<sub>7</sub><sup>•</sup>, Ph<sup>•</sup>, PhOCH<sub>2</sub><sup>•</sup>, OH<sup>•</sup>, and PhO<sup>•</sup>.

5. Modeling in the 998–1020 K region. In the higher temperature region, where a capillary reactor was used, two adjustments were made to our model, to account for anisole decomposition and the major products: benzene, CO, phenol, and methane:  $k_{14}$  (recombination of PhO<sup>•</sup> + H<sup>•</sup>) was lowered with a factor of 17 to  $6 \times 10^{11}$  M<sup>-1</sup> s<sup>-1</sup>. And  $k_{15}$  (reaction of methyl with hydrogen) was taken as determined by Warnatz.<sup>34</sup> The parameters of Schatz<sup>35</sup> resulted in a methyl concentration too high to rationalize the yield of ethane (see Figure 11 for modeling results).

The results are less accurate than in the low temperature region, especially for benzene, CO, and dibenzofuran production. Minor adjustments of reactions T-10, T-15, and T-19 (e.g., a change in the temperature dependence) could deal with this.

A modeled rate constant of  $6 \times 10^{11}$  for the recombination of phenoxyl and H shows that this system is more "well-behaving", although this value still appears to be too high for gas-phase recombination (see Discussion).

### Discussion

Modeling can increase the insight in the reactions taking place but at the same time may raise new questions. In this modeling study concentration levels of methyl and phenoxyl radicals are easy to estimate, ethane being a direct measure for methyls and dibenzofuran and cresols (at low conversions) for phenoxyl. For H<sup>•</sup> a concentration level around  $10^{-11}$  M has been inferred. This estimation is fairly accurate because it is directly related to the rate of induced decomposition of anisole.

The methyl radical concentration is regulated by reaction with  $H_2(15)$ , generating H-atoms. The problem now is to control the H-flux, by assessing its disappearance pathways. Note that [H•] derived from our model calculations,  $(2-4) \times 10^{-11}$  M at 793-873 K, is 10<sup>2</sup> times the equilibrium concentration in 0.5 atm of hydrogen.<sup>41,42</sup> The main reactions that determine the H-atom concentration, besides reaction 14, appear to be reactions 1, 15, and 23. Recombination of H-atoms (third body needed) is negligible at these concentration levels. Removal through formation of H-arene adducts can be ruled out because of the low stability of cyclohexadienyl radicals at the temperatures applied. We have chosen to increase the rate of recombination of phenoxyl and H<sup>•</sup>, although gas-phase chemistry cannot account for this. The hydrogenolysis study was extended to higher temperatures to validate the fitted reaction rates. Here the H-atom flux seems to be better controlled; for  $k_{14}$ , now a value of  $6 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ suffices, although the difference in H<sup>•</sup> concentration ( $6 \times 10^{-9}$ M) with the equilibrium value still amounts to a factor  $10^2$  at 1003 K.

As to the fast decay of H<sup>•</sup> and PhO<sup>•</sup>, it is a well-known phenomenon that quartz reactors absorb H-atoms and catalyze the recombination of H<sup>•</sup>. Numerous studies<sup>43,44,45</sup> of these reactions have been made, mostly at temperatures <500 K, in which the Rideal mechanism is preferred as exemplified by reactions 25 and 26. Here W<sub>0</sub> represents an empty adsorption

$$H^{\bullet} + W_{0} \Leftrightarrow W - H$$
 (25)

$$W-H + H^{\bullet} \leftrightarrow W_0 + H, \qquad (26)$$

site and W-H a surface adsorbed H-atom. The sum of these processes has been approximated generally as a single reaction (27) and first-order rate constants have been reported. Absolute

$$\mathrm{H}^{\bullet} \to ^{1}/_{2}\mathrm{H}_{2} \tag{27}$$

values will strongly depend on pressure, temperature, and geometry and S/V ratios of the reactor. Above 500 K reaction 25 becomes proportional to H<sup>•.43</sup> Ahumada and Michael<sup>44</sup> reported  $k_{27} = 21 \text{ s}^{-1}$  at 470 K and 700 Torr of H<sub>2</sub> (quartz reactor with  $S/V = 0.29 \text{ cm}^{-1}$ ); Kanan et al.<sup>46</sup> reported an experimental  $k_{27}$  value of >10<sup>4.2</sup> s<sup>-1</sup> near 773 K in a Pyrex reactor for the pyrolysis of propane, where the surface was treated with NaOH, which is known to improve wall recombination reactions.

In our experiments "H" in reaction 26 could well be replaced by phenoxyl,

$$W-H + PhO^{\bullet} \Leftrightarrow W_0 + PhOH$$
 (28)

When speaking in terms of first-order decay constants,  $k_{27}$  is complementary with [PhO<sup>•</sup>] $k_{14} = k'_{14}$ , with  $k_{14}$  the modeled rate constant for recombination of H and phenoxyl. At 823 K  $k'_{14}$ = 10<sup>5.5</sup> s<sup>-1</sup> and at 1010 K  $k'_{14} = 10^{5.6}$  s<sup>-1</sup>.

From this perspective, wall decay of H-atoms has the same decay throughout the temperature range 793-1020 K. The fact that the S/V ratio at 1010 K is 19 times higher than at 823 K  $(S/V = 57 \text{ and } 3.1 \text{ cm}^{-1}, \text{ respectively})$  is probably compensated by the higher *reverse* rate constant of reaction 25 at this temperature.

Phenoxyl decomposition proves to be much too slow to account for CO formation accompanied by  $C_5H_6$ , even in the hightemperature region. We chose not to correct for the parameters of Lin (see Introduction), because a factor 100 had to be fitted for, with a low-temperature dependence, and that would not be realistic. Alternative mechanisms probably involve interaction of H-atoms. A direct way to do this could be reaction of PhO<sup>•</sup>





SCHEME VI: Alternative Mechanism for Formation of CO through Attack of H<sup>•</sup> at a "Meta" Position of Anisole



with H<sup>•</sup> to get CO and a C5-species, but it would require a totally unrealistic rate constant >  $10^{12} M^{-1} s^{-1}$ . A good possibility may be through reaction with ketophenol, formed in reactions 14 (PhO<sup>•</sup> + H<sup>•</sup>) and 23 (PhOCH<sub>3</sub> + H<sup>•</sup>). In the case of equilibration with phenol, the ratio of ketophenol/phenol will be  $3 \times 10^{-2}$  at 823 K, and, with a required overall rate for CO formation by reaction  $24 of 3 \times 10^{-6} M s^{-1}$ , the rate constant for H-addition to ketophenol would exceed  $1 \times 10^{11} M^{-1} s^{-1}$ , which is not likely. But if conversion of ketophenol into phenol is slow,<sup>26</sup> the ketophenol concentration will be higher and H-addition is conceivable (Scheme IV). A third possibility is for ketophenol to decompose in a unimolecular way (Scheme V). Taking 1,3,5,hexatriene into 1,3,cyclohexadiene as an example, the first step in Scheme V would require an activation energy of around 60 kcal/mol.<sup>30</sup>

The latter two scenarios require ketophenol to be a long lived species. This may well be the case, as direct enolization is an orbital symmetry forbidden process.<sup>26</sup> Note further that the Claisen rearrangement of allylphenyl ether to *o*-allylphenol is blocked in the gas phase,<sup>10,47</sup> the second, enolization step—and therefore the overall reaction—appeared to proceed only with the help of a large surface-to-volume ratio or of a catalyst such as acetic vapor. In our case we are as yet unable to substantiate the presence of ketophenol and assess its concentration; it will rapidly enolize after leaving the reactor.

Another possibility is reaction of H<sup>•</sup> with anisole itself, to result in CH<sub>3</sub>•, CO, and cyclopentadiene (Scheme VI). To get the "right" bicyclic intermediate H-addition at the meta position is needed followed by methyl elimination. However the  $\Delta H_f$  of intermediate C is estimated as high as 28 kcal/mol, and therefore this reaction would overall be 29 kcal/mol endothermic and not feasible.

As to the toluene carrier technique, previously determined Arrhenius parameters by this method<sup>48</sup> are used to give low preexponential factors, as, e.g., in ref 1. In this study we have demonstrated that with current gas chromatographic techniques and with the choice of an ample excess of radical scavenger, this technique is just as accurate as, e.g., VLPP.

#### Conclusions

The hydrogenolysis of anisole is dominated by initial cleavage of the PhO-CH<sub>3</sub> bond. The rate constant for this bond cleavage was independently determined by the *p*-fluorotoluene carrier technique as  $k_1 = 10^{15.3(\pm 0.2)} \exp[(-63.6(\pm 0.7) \text{ kcal mol}^{-1})/RT]$ (s<sup>-1</sup>). These parameters are in very good agreement with currently accepted values and thermodynamic considerations. On this basis the calculated heat of formation at 298 K of the phenoxyl radical is 12.1 kcal/mol. The extra amount of methane is the result of a displacement reaction of H-atoms with the p-fluorotoluene which is corroborated by the occurrence of fluorobenzene.

The methyl radicals generated in a hydrogen atomsphere are replaced by H-atoms and create an environment in which no compound is completely stable. At 823 K, around 40% (decreasing to 15% at high conversions and high temperatures) of the conversion of anisole is accounted for by H-atoms, resulting not only in anisyl (PhOCH<sub>2</sub>) radicals which end up as benzene and CO, but also leading to phenol directly. This latter, new, reaction of H<sup>•</sup> with anisole to result in (keto)phenol and methyl was called for after extensive modeling and might also be an explanation for the phenol formation in the system of Mackie and Doolan.<sup>11</sup>

Another important species is the phenoxyl radical. Decomposition, though, to CO and the cyclopentadienyl radical is not important at all in our system! The major role of phenoxyl is to scavenge H-atoms. The main route to CO and cyclopentadiene is proposed to be conversion of ketophenol, whether by H-atoms or via direct, molecular reactions.

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## Appendix A: On the Heat of Formation of the Phenoxyl Radical

From the activation energy of reaction 1, the thermal decomposition of anisole,  $\Delta H_i$ , of PhO<sup>•</sup> can be determined.

The enthalpy of reaction 1 at 823 K (in the middle of the temperature region) is given, when accepting zero activation energy for the back-reaction and working with concentration units, as  $\Delta H_r(823 \text{ K}) = E_a + RT = 63.6 + 1.6 = 65.2 \text{ kcal mol}^{-1}$ .

With  $\Delta C_p$  for reaction 1 being approximately zero over the temperature range considered (estimated by group additivities), it follows that  $\Delta H_f(298 \text{ K}) = 65.2 \text{ kcal mol}^{-1}$ . From the enthalpy balance  $\Delta H_f(\text{PhO}^{\bullet}) = \Delta H_f(\text{PhOCH}_3) + \Delta H_f(298 \text{ K}) - \Delta H_f(\text{CH}_3^{\bullet})$ , and, with  $\Delta H_f(\text{PhOCH}_3) = -18.0^{21} \text{ and } \Delta H_f(\text{CH}_3^{\bullet}) = 35.06^{49} \text{ kcal/mol}, \Delta H_f(\text{PhO}^{\bullet}) = 12.1 \text{ kcal mol}^{-1}$  is calculated.

When 3 kcal/mol is taken as the energy needed for the backreaction as proposed by Lee,<sup>50</sup> the  $\Delta H_f$  for PhO<sup>•</sup> would descend to 9.1 kcal/mol. In the literature, values from 9–13.2 kcal mol<sup>-1</sup> have been advanced. In 1982 McMillen and Golden<sup>49</sup> evaluated a value of 11.4 kcal/mol based on the decomposition of ethoxybenzene obtained by Colussi et al.<sup>10</sup> However, when the current value for  $\Delta H_f$  for ethyl (28.4 kcal/mol)<sup>51</sup> is applied, the heat of formation of phenoxyl descends to 9.4 kcal/mol. Mulder et al.<sup>52</sup> and Back<sup>53</sup> proposed values in the same range, 9.0 and 9.6 kcal/mol, respectively. Recently however, Tsang<sup>54</sup> obtained from the decomposition of *n*-butylphenylether a value of 13.2 kcal/mol.

## Appendix B: Calculation of the Concentrations of H<sup>•</sup>, CH<sub>3</sub><sup>•</sup>, and FPhCH<sub>2</sub><sup>•</sup>

The amount of free hydrogen atoms can be estimated from the production of fluorobenzene according to reaction 8. The rate constant for displacement of CH<sub>3</sub>• in fluorotoluene is taken to be equal to that for the corresponding reaction in toluene; i.e.,  $k_8 = 1.2 \times 10^{10} \exp[(-5 \text{ kcal mol}^{-1})/RT] \text{ M}^{-1} \text{ s}^{-1}.^{18b}$  On this basis [H•] is found to vary from  $10^{-13}-10^{-12}$  M between 793 and 873 K.

 $[CH_3^{\bullet}]$  can be extracted from the rate of formation of  $CH_4$  according to the next reaction

$$CH_3^{\bullet} + FPhCH_3 \rightarrow CH_4 + FPhCH_2$$

With<sup>55</sup>  $k = 10^9 \exp[(-8 \text{ kcal mol}^{-1})/RT] \text{ M}^{-1} \text{ s}^{-1}$ , [CH<sub>3</sub>\*] changes from  $2 \times 10^{-11}$  to  $2 \times 10^{-10}$  M.

Concerning the fluorobenzyl radical concentration, especially at high degrees of anisole conversion (and high temperatures), the amount of bibenzyl in the reactor is at equilibrium with the corresponding benzyl radicals:

### $2FPhCH_2^{\bullet} \Leftrightarrow FPhCH_2CH_2PhF$

For example at T = 873 K and given  $K(eq) = 2.7 \times 10^{-10}$  M (K =  $1.6 \times 10^5 \exp[(-59 \text{ kcal mol}^{-1})/RT]$  M for unsubstituted bibenzyl<sup>56</sup>), the fluorobenzyl radical concentration amounts to ca.  $2 \times 10^{-8}$  M.

### Appendix C: Back-Reactions in Model

Our kinetic model does not include back-reactions automatically. For only three reactions, the reverses are incorporated, namely, T-1  $\leftrightarrow$  T-9, T-2  $\leftrightarrow$  T-17, and T-5  $\leftrightarrow$  T-16. For these three pairs of reaction, microscopic reversibility is accounted for. As to the other 31 reactions, these can be divided in four groups:

I. There are decompositions to give two species. Back-reactions are not feasible. To this class of reactions belong T-4, T-14, T-27, T-32, and T-33.

II. Back-reactions with PhOCH2 and OH can be disregarded because their concentrations are in the order of 10<sup>-13</sup> M. This excludes T-3, T-6, T-13, T-18, and T-21.

III. There are recombinations to give stable molecules. The back-reactions that have bond dissociation energies > 80 kcal/ mol are not important under our conditions. This eliminates reactions T-7, T-8, T-10, T-11, T-24, T-25, T-28, T-29, T-30, T-31, and T-37.

IV. As to the rest T-15, T-26, and T-36 are bimolecular reactions that lead to three species. As to T-34, the backreaction: H-abstraction from benzene, has a rate constant of 2.2 × 10<sup>7</sup> M<sup>-1</sup> s<sup>-1</sup> at 823 K ( $k_{-34} = 10^{9.5} \exp[(-8.1 \text{ kcal mol}^{-1})/RT]$  $M^{-1}$  s<sup>-1</sup>);<sup>57</sup> applying the concentrations in Table VI makes the forward rate 90 times faster. The rate constant for  $H^{\bullet} + H_2O$ . the reverse of T-35 amounts to  $2.4 \times 10^5$  M<sup>-1</sup> s<sup>-1</sup> at 823 K (with  $k_{-35} = 4.6 \times 10^5 T^{1.6} \exp[(-18.6 \text{ kcal mol}^{-1})/RT] \text{ M}^{-1} \text{ s}^{-1}$  as ref 34), making the forward rate even  $2.3 \times 10^4$  times faster.

For T-22 and T-23 would the reverse reactions be just as fast as reactions T-25 and T-26. However they are all very slow and do not have an effect on the other products or overall conversion.

For T-12, T-19, and T-20, the rate constants for the reverse reactions were calculated from thermodynamic parameters.  $k_{12}$ =  $10^8 \exp[(-27.4 \text{ kcal mol}^{-1})/RT] \text{ M}^{-1} \text{ s}^{-1}, k_{-19} = 10^8 \exp[(-15.7 \text{ kcal mol}^{-1})/RT]$ kcal mol<sup>-1</sup>)/RT] M<sup>-1</sup> s<sup>-1</sup>, and  $k_{-20} = 10^{8.1} \exp[(-15.1 \text{ kcal mol}^{-1})/RT]$  M<sup>-1</sup> s<sup>-1</sup>. With the concentrations from modeling results (Table VI), it can be derived that  $v_f/v_r$  is 100 in the case of T-20 and over  $10^5$  for T-12 and T-19.

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