Summary

Experimental studies show that relative abstraction/arylation rates of polycyclic aromatic aryl radicals with toluene depend significantly on the structure of the aryl radical. Under the present conditions, the 9-anthracenyl radical, for instance, is about 15 times less likely to arylate toluene than is the phenyl radical. Relative rates of arylation at the different positions in toluene and naphthalene, on the other hand, are the same for all aryl radicals studied.

This behavior is interpreted to be a direct consequence of the reversibility for the addition of aryl radicals and the resulting sensitivity to differences in arylation thermodynamics. Theoretical analysis suggests that the thermodynamic differences arise primarily from inherent differences in stabilities of the aryl radicals as measured by differences in arene C–H bond strengths. It also indicates that, on the basis of bond strengths, three types of aryl radicals can be distinguished, typified by phenyl, 1-naphthalenyl, and 9-anthracenyl radicals. The size of the aromatic network has little if any effect on bond strengths. Instead, effects can be interpreted as a consequence of the local σ-bonding environment.

Acknowledgment. This work was supported by a grant from the Gas Research Institute.

Registry No. Toluene, 108-88-3; phenyl, 2396-01-2; 1-naphthalenyl, 2510-51-2; 2-naphthalenyl, 10237-50-0; 9-anthracenyl, 27735-77-9; hydrogen, 1333-74-0; naphthalene, 91-20-3; 9-phenanthrenyl, 20199-82-0; 9-tetracenyl, 61062-92-8; 1-pyrenyl, 27735-78-0; 2-pyrenyl, 61062-84-8; 3-pyrenyl, 27735-78-0; 9-pentacenyl, 118017-21-3; benzene, 71-43-2; anthracene, 120-12-7; phenanthrene, 85-01-8; naphthacene, 92-24-0; pyrene, 129-00-0; pentacene, 135-48-8.

The Thermal Decomposition of Hydroxy- and Methoxy-Substituted Anisoles

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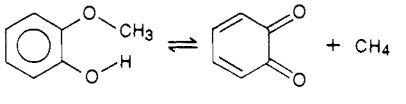
Abstract: Rates of decomposition of anisole and the three isomeric hydroxyanisoles and methoxyanisoles along with phenetole (ethoxybenzene) and *o*-hydroxyphenetole were determined in a very low pressure pyrolysis apparatus. In all reactions, the predominant process was O–methyl bond homolysis. Therefore, relative rates provide a quantitative measure of the effects of hydroxy and methoxy substituents on bond strengths in anisoles. A large bond-weakening effect was observed for the *o*-hydroxy group (7 kcal mol^{-1}), accounting for the exceptional lability of guaiacol observed in the condensed-phase studies of both Vuori and Virk. The *p*-hydroxy group weakened the anisole O–methyl bond by 2.5 kcal mol^{-1} and meta substitution had little effect. Both *o*- and *p*-methoxy groups weakened the O–methyl bond by 4 kcal mol^{-1} and *m*-methoxy substitution weakened this bond by 1 kcal mol^{-1}. Rates of all the reactions, when extrapolated to lower temperatures, were similar to rates of condensed-phase thermolysis reactions, indicating that homolysis is a key step in the liquid phase reactions. Other findings and conclusions are as follows: (1) Measured substituent effects do not correlate well with published rates of H abstraction from substituted phenols. (2) Bond breaking in anisoles occurs in a direct manner, without initial migration of the methyl group to the ring. (3) The generally observed higher reactivity of *o*-quinones than *p*-quinones may be due, in large part, to the special stabilization of the *o*-hydroxyphenoxy radical. (4) Theoretical (AM1) calculations yield the correct magnitude of the measured bond-weakening effects, but they do not reproduce important trends.

I. Introduction

Thermal decomposition reactions of substituted anisoles are of considerable current interest for two quite different reasons. First, since these structures are thermally labile constituents of lignin, their decomposition reactions serve as models for the pyrolysis of biomass and coal.[1-7] Second, homolysis rates of these molecules yield thermodynamic effects of substituents on bond strengths. Related substituent effects influence the effectiveness of phenolic antioxidants such as vitamin E[8] and BHT.[9]

Liquid-phase thermolysis studies by Vuori,[1] Bredenberg,[2-4] Schlosberg,[5], Virk,[6] and their co-workers of the decomposition of methoxy- and hydroxy-substituted anisoles and related compounds show that rates depend strongly on the position of substitution and that guaiacol (*o*-hydroxyanisole) is exceptionally labile. Sizable substituent effects were also found for *o*- and *p*-methoxyanisoles, although the reactivities of these were comparable. On the basis of the exceptionally rapid rate of decomposition of guaiacol, Klein and Virk[6] proposed the occurrence of a facile concerted reaction (reaction 1) in which methane and



(1)

o-quinone are formed directly, without the intermediacy of free radicals. However, more recently Vuori,[1] on the basis of measured relative spin concentrations in the pyrolyzed products, concluded that the concerted path made only a minor contribution. The nature of these initial products is of some significance to biomass and coal chemistry, since an inert species (methane) is generated in one case and a reactive intermediate (methyl radical) is formed in the other.

Most of the available data on the thermodynamics of phenoxy radicals comes from the work of Mahoney and co-workers.[10,11] Their work shows that substituents can have quite large effects. Further, for the series of molecules studied, they reported a strong correlation between rates of hydrogen abstraction from substituted phenols and phenolic O–H bond strengths. Partly on the basis

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of this work, Ingold and co-workers have explained the special effectiveness of Vitamin E as an antioxidant as a consequence of the thermodynamic effects of substituents.[8] However, abstraction rates are also well correlated by the σ^+ substituent parameter,[12] suggestive of polar effects,[13] and there is presently some debate concerning the relative importance of thermodynamic and polar effects in H-abstraction reactions.[8,10,11,13-18]

In the present work, we report rates and products of the gas-phase unimolecular decomposition of anisole and the three isomeric hydroxyanisoles and methoxyanisoles. In addition, to test various mechanistic possibilities, we examined the decomposition of phenetole (ethoxybenzene), *o*-hydroxyphenetole, *o*-bromoanisole, and *o*-chloroanisole.

All experiments were done by using the very low pressure pyrolysis (VLPP) technique.[19,20] The low densities of these experiments served to eliminate radical-induced decomposition reactions. Mass spectrometric detection allowed the detection of free-radical products. Recently, on the basis of gas phase ion thermodynamics, Beauchamp and co-workers[21] have obtained bond strengths for the benzylic C–H bond in toluene and the xylenes that were in excellent agreement with VLPP values[22] (the average deviation in the two sets of relative bond strengths was ±0.2 kcal mol^{-1}). This supports the idea that VLPP can yield highly accurate values for substituent effects.

II. Experimental Section

Details of the VLPP technique have been given in earlier publications.[19,20,22-24] The reactor used for the present studies was a single exit aperture quartz cell (cross sectional area = 9.1 mm^2), 75 cm^3 in volume, with a collision number of 1160. Its temperature could be varied between 300 K and 1275 K and was measurable to ±3 K accuracy with a precision of better than 1 K with three chromel alumel thermocouples placed near different regions of the reactor.

The VLPP reactor had two inlets. The reactant gas entered through one of these. An inert gas such as argon flowed continuously through the second inlet at a measured flow rate. All mass spectral peaks in this study were normalized to the peak height of the inert gas. In order to determine response factors, the gases of interest were introduced through a separate, heated Knudsen cell.[20] Pressures inside this cell were monitored directly with a pressure transducer. Flows were computed from measured pressure, molecular weight of the flowing gas, temperature, and exit-aperture size.

Products were analyzed with a quadrupole mass spectrometer operating at 20 eV. For rate measurements, in order to achieve a better signal-to-noise ratio, a separate quadrupole mass analyzer operating at an ionization energy of 70 eV was used. All necessary reagents were obtained from commercial sources and were degassed until a constant vapor pressure was obtained. Flows of reactant were adjusted to maintain Knudsen flow conditions in the reactor (<10^{-3} Torr).

III. Results

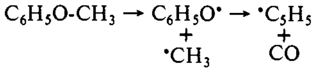
A. Products. The mass spectra of reaction products indicated that for all reactions the initial step is homolysis of the alkoxy C–O bond. To illustrate the mass spectra observed, results of several studies are given in Table I and the results are discussed below.

Table I. Percent Mass Spectral Intensities (at 20 eV) Observed from the Reaction Products of Selected Anisoles

		relative peak intensities		
m/e	probable species	anisole (1210 K)[a]	*p*-hydroxy-anisole (1200 K)[a]	guaiacol (1165 K)[a]
15	CH_3	38	79	80
16	CH_4	9	18	17
28	C_2H_4/CO	100	100	100
30	C_2H_6			4
65	C_5H_5	18		
81	C_5H_4OH		13	30
93	C_6H_5O	1		
94	C_6H_5OH	3		
109	$C_6H_4(OH)O$		8	
110	$C_6H_4(OH)_2$		43	35
P	Parent	4	2	3

[a] T_R, the reactor temperature at which reaction products were analyzed. The extent of reaction in each case was greater than 95%.

(i) Anisole. At 20 eV, three major product peaks were observed, *m/e* = 15, 28, and 65. Minor peaks (i.e., less than 10% of the largest product peak: *m/e* = 28) were observed at *m/e* = 16, 93, and 94. The peak at *m/e* = 15 is that of methyl radicals. Previous studies have also shown that they are easily detected under VLPP conditions.[20] The peaks at 93 and 94 are indicative of phenoxy radicals. Colussi et al.[25] reported that phenoxy radicals decompose in VLPP experiments via decarbonylation to CO (*m/e* = 28) and cyclopentadienyl radicals (C_5H_5, *m/e* = 65). They also abstract H atoms from surfaces to form phenol (*m/e* = 94). On the basis of the above mass spectra, we conclude that the primary step in the thermal decomposition of anisole is O–CH_3 bond homolysis (reaction 2) to form methyl (*m/e* = 15) and phenoxy (*m/e* = 93)

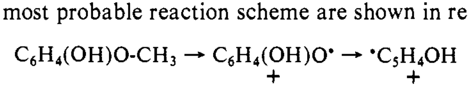


$$C_6H_5O\text{-}CH_3 \rightarrow \underset{\cdot CH_3}{\overset{}{C_6H_5O^\cdot}} \rightarrow \underset{CO}{{}^\cdot C_5H_5} \qquad (2)$$

$$\text{(i.e., } C_6H_5O\text{-}CH_3 \rightarrow C_6H_5O^\cdot + {}^\cdot CH_3 \rightarrow {}^\cdot C_5H_5 + CO)$$

radicals. The minor peak at *m/e* = 16 is presumed to be methane formed by H abstraction from surfaces by methyl radicals. The ratio of methane to methyl peak intensities remained rather constant (1/4–1/6) over a wide range of flow rates and ionization energies. Also, these relative intensities were similar to those found in previous studies of ethylbenzene dissociation,[24] where methyl radicals were clearly established as the primary products.

(ii) Hydroxyanisoles. Mass spectra of products of the decomposition of the three hydroxyanisoles (20 eV) were very similar. They all showed major product peaks at *m/e* = 15, 16, 28, 81, and 110 with a minor one (less than 10% in intensity of the largest product peak: *m/e* = 28) at *m/e* = 109. The peak assignments and the most probable reaction scheme are shown in reaction 3.



$$C_6H_4(OH)O\text{-}CH_3 \rightarrow \underset{+\ {}^\cdot CH_3}{C_6H_4(OH)O^\cdot} \rightarrow \underset{+\ CO}{{}^\cdot C_5H_4OH} \qquad (3)$$

Just as for the reaction of anisole described above, the initial step is O–CH_3 bond homolysis to form methyl (*m/e* = 15) and hydroxyphenoxy (*m/e* = 109) radicals. The latter then either abstract H atoms to form dihydroxybenzenes (*m/e* = 110) or decarbonylate to products with *m/e* = 28 and 81. Importantly, the ratio of the relative intensities of the *m/e* = 16 and *m/e* = 15 peaks for each reaction was 1/4, the same as found for anisole.

(iii) Other Product Studies. Product mass spectra (20 eV) of the methoxyanisoles, *o*-chloroanisole, and *o*-bromoanisole showed no anomalies, indicating that they too decomposed through an initial O–CH_3 bond homolysis, forming methyl and the corresponding substituted phenoxy radicals. However, in view of the extensive dissociation of product phenoxyl radicals and possible ion fragmentation (Table I), a clear mechanistic distinction between initial halogen or methyl loss could not be made on the basis of these mass spectral measurements.

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Table II. Results of Flow-Rate Studies of Some Anisoles

compound	T_R, K	flow rate, molec $s^{-1} \times 10^{14}$	% dec
anisole	1092	3.9	71
		4.6	70
		5.0	70
		7.0	70
		9.4	69
		13	70
guaiacol	954	17	73
		29	74
		38	74
		73	73
		2.0×10^2	74
p-hydroxyanisole	1005	14	62
		16	62
		22	62
		29	62

Product studies of phenetole have been reported by Colussi et al.[25] and they were done here only at 70 eV. Products of phenetole showed major peaks at m/e = 27, 28, and 29 with minor ones (<10%) at 30, 65, 93, and 94. The major mass spectral peaks in the pyrolysis of *o*-hydroxyphenetole were also at m/e = 27, 28, and 29. Minor peaks were observed at m/e = 30, 81, 109, and 110. This is consistent with phenetole and *o*-hydroxyphenetole decomposing through an initial O–ethyl bond homolysis. Product ethyl radicals are primarily converted to ethane (m/e = 28). In both reactions, the ratio of m/e = 28 and 27 peaks was similar to that for ethene, indicating that ethene was formed substantially faster than CO.

B. Rate Measurements and Calculations. Empirical unimolecular decomposition rate constants, k_{uni}, were calculated from eq 4, where f is the fraction of reactant decomposed and k_e, the

$$(k_{\text{uni}}/k_e) = f/(1-f) = (I_0 - I)/I \qquad (4)$$

escape rate constant, equals $3.965(T/M)^{0.5}$ (M/amu = molecular weight and T/K = temperature) for our 3-mm-aperture reactor.[24] The fraction of reactant remaining, $1-f$, at any temperature, T, is directly proportional to the mass spectrometer signal intensity, I, of the parent molecular ion. Rates for selected reactions (anisole and *o*- and *p*-hydroxyanisole) were measured over a range of flow rates and found to be flow independent (Table II), confirming the unimolecularity of the reaction. Also, at any temperature in the range studied, the percent decomposition was reproducible to ±1%.

The unimolecular reactions studied are in the falloff (collision-frequency-dependent) region, and the degree of falloff varies slightly from reaction to reaction. Therefore, measured relative rates depend on collision frequency. To eliminate this dependence, RRKM calculations[26] were used to convert observed rate constants to high-pressure values, k^{∞}. These calculations used A factors of $10^{15.5}$ s^{-1} per methoxy group, which was based on an assumed reverse rate constant of $10^{9.5}$ M^{-1} s^{-1} and estimated reaction entropies.[25] The vibrational models employed for the calculations were derived from a previously reported model for ethylbenzene.[26] They were adjusted so that the entropies and heat capacities of reactants matched the values calculated by group additivity.[27] Activation energies were adjusted in RRKM models to match the observed low-pressure rate constants.

In figures 1–4 are shown the VLPP rate constants for the unimolecular decomposition all the compounds examined in this work along with RRKM fits to the data (solid lines). Close fits of the RRKM curvatures with experimental data confirms the homogeneity and unimolecularity of these reactions. Derived bond-dissociation energies relative to anisole (ΔBDE) are summarized in Table III. Because of the assumption of constant A factors per methoxy group, ΔBDE is more precisely a measure of differences in ΔG rather than ΔH for bond dissociation.

Table III. Differences in $O-CH_3$ Bond Dissociation Energies of Substituted Anisoles Relative to That of Anisole[a]

	substituent position					
	ortho		meta		para	
substituent	exptl	calcd[b]	exptl	calcd	exptl	calcd
OH	*−7.2*	−6.0	*0.3* 2.6[c]	0.6	*−2.5* −3.7[c]	−4.0
OCH_3	*−4.2*	−5.3[e]	*−1.0*	0.1	*−3.9* −4.3[d] −5.9[f]	−4.1
Cl	*−2.2*	−0.9		1.0		0.5
Br	*−1.7*	−0.6		0.7		0.9

[a] Results of the present experiments are in italic. BDE (kcal mol^{-1}) of anisole: 64.7 (exptl); 66.3 (calcd). [b] Calculation by the AM1 method.[42,43] Differences in O–H BDEs of substituted phenols relative to that of phenol (88.3 kcal mol^{-1}) from ref 11. [c] Via Brønsted relationship. [d] From equilibrium constant. [e] Values for the more stable trans isomer. [f] Mulder et al.[45]

Table IV. Results of the Study of the Decomposition Pathway of Hydroxyanisoles and *o*-Hydroxyphenetole

reactant	T_R, K[a]	% methane or ethane formed
o-hydroxyanisole	1057	16[b]
m-hydroxyanisole	1177	18[b]
o-hydroxyphenetole	1055	8[c] (7[d])
phenetole	1117	3[c] (4[d])

[a] Over 90% of the reactant decomposed at these temperatures. [b] Percent methane formed/decomposed reactant. [c] Percent ethane formed/decomposed reactant. [d] From ethane/ethene ratio.

Table V. Rate Constants for Anisole Decomposition (k_1^{∞}/s^{-1})

T_R, K	*a*	*b*	*c*
795	5.7×10^{-3}	11×10^{-3}	9.7×10^{-3}
762	1.2×10^{-3}	2.0×10^{-3}	2.0×10^{-3}
740	3.7×10^{-4}	5.8×10^{-4}	6.6×10^{-4}
720	1.2×10^{-4}	1.2×10^{-4}	2.2×10^{-4}

[a] Rate parameters from ref 28; log A = 13.7 s^{-1}, E_a = 58.0 kcal mol^{-1}. [b] Recommended rate parameters from present studies; log A = 15.5 s^{-1}, E_a = 63.5 kcal mol^{-1}. [c] Rate parameters from present studies assuming A factor from ref 28; log A = 13.7 s^{-1}, E_a = 57.4 kcal mol^{-1}.

In order to derive the upper limit for the contribution of concerted reactions to the decomposition of guaiacol, we measured the yield of methane in the decomposition of guaiacol and *m*-hydroxyanisole, the latter being a reference, for it cannot yield methane in a conventional concerted reaction. In both cases the flow of methane detected represented about 17% of the decomposed reactant (Table IV). As noted earlier, a substantial fraction of this methane may originate from H abstraction by methyl radicals from surfaces. Any contribution of the concerted reaction to guaiacol decomposition must be significantly less than 17%.

To provide further confirmation that the *o*-hydroxy group does not open up a concerted channel, we measured the yield of ethane in the decomposition of phenetole and *o*-hydroxyphenetole (*o*-ethoxyphenol). Ethane would be the product of a concerted mechanism, while ethene is a product of a homolysis reaction. Ethane is a minor product in both reactions, being formed ca. 5% faster in the *o*-hydroxyphenetole reaction (Table IV). Equivalent results were derived for the ratio of ethene to ethane with the mass 27 peak as a measure of ethene flow (its parent coincided with CO, another possible reaction product).

IV. Discussion

A. Anisole Decomposition. Our unimolecular rate constants for the decomposition of anisole, together with the RRKM fit to the data, are presented in Figure 1. The resulting high-pressure rate expression is $k_1/s^{-1} = 10^{15.5} \exp(-63.5 \text{ kcal}/RT)$. Using the toluene-carrier technique, Paul and Back[28] reported that the decomposition of anisole proceeded cleanly by O–methyl bond

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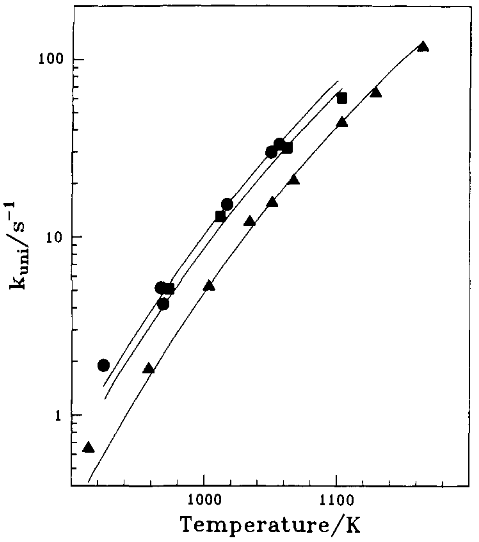


Figure 1. Rate constants measured from the thermal decomposition of (▲) anisole, (■) *o*-bromoanisole, and (●) *o*-chloroanisole. The solid lines are RRKM fits to the data.

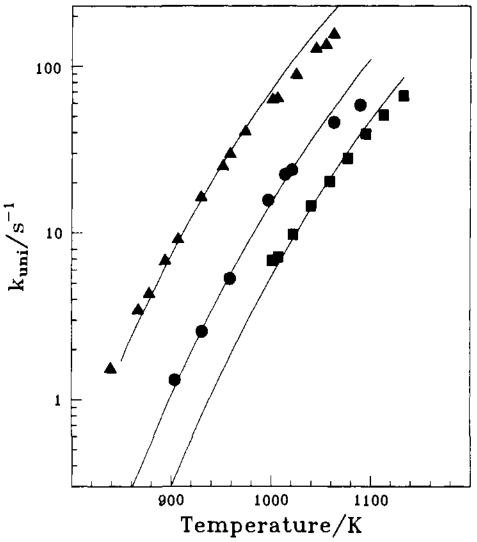


Figure 2. Rate constants measured from the thermal decomposition of the three isomeric hydroxyanisoles; (▲) ortho, (■) meta, (●) para. The solid lines are the RRKM fits to the data.

homolysis with k_1/s^{-1} = $10^{13.7}$ exp (−58.0 kcal/RT) in the 720–795 K temperature range. As shown in Table V, rates are in reasonable agreement when the present results are extrapolated to their temperature range.[27]

In the present work we prefer not to use the "low" Arrhenius parameters obtained by Paul and Back,[27] since they lead to the prediction that the methyl-phenoxyl recombination rate is $10^{8.3}$ M^{-1} s^{-1}, which is significantly outside the "normal" range of $10^{9.0}$–$10^{10.0}$ M^{-1} s^{-1}. Only modest systematic errors at the temperature extremes of their experiments could cause an error of this magnitude.[29] In any case, the *relative* activation energies and high-pressure rate constants of primary interest in this work are rather insensitive to the value chosen for the A factor.

B. Hydroxyanisoles. Rate data for *o*-, *m*-, and *p*-hydroxyanisoles along with RRKM fits to the data shown in Figure 2 and ΔBDE values are given in Table III. Bond weakening caused by the *o*-hydroxy group is exceptional. Since odd-electron density in the phenoxyl radical is smaller in the ortho than the para position,[30,31] an upper limit of a 2.5-kcal contribution (the para value) may be attributed to the electronic stabilization of *o*-hydroxyphenoxy radical, leaving at least 4.7 kcal of additional stabilization.

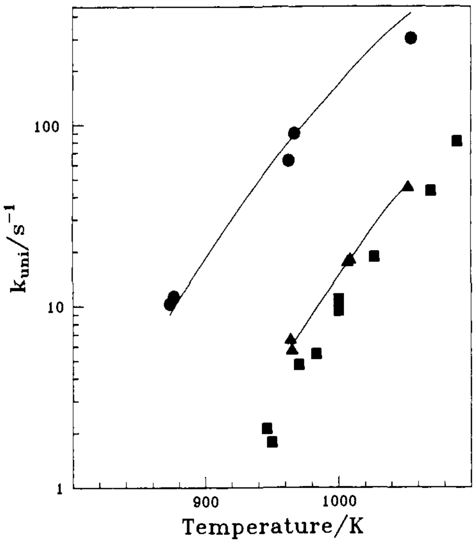
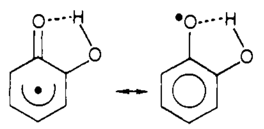


Figure 3. Rate constants measured from the thermal decomposition of (▲) phenetole (ethoxybenzene) and (●) o-hydroxyphenetole; (■) are data from ref 25. The solid lines are RRKM fits to our data.

We now examine the possibility that this additional stabilization arises from relief of repulsion in guaiacol. Unfortunately, no heat of formation data is available for guaiacol, but data is available for related disubstituted hydroxy- and methoxybenzenes.[32-36] For the disproportionation reaction 2PhOH → Ph(OH)$_2$ + PhH (I), enthalpies for ortho, meta, and para substitution are 1.4, 0.1, and 2.4 kcal mol^{-1}. The enthalpy for 2PhOCH$_3$ → *o*-Ph(OCH$_3$)$_2$ + PhH (II) is only −0.9 kcal mol^{-1}. Given that neither *o*-dihydroxy or *o*-dimethoxybenzene shows substantial substituent destabilization, it seems possible that little exists also in the cross hydroxy/methoxy compound, guaiacol.

To explore this matter further, we carried out a series of AM1 calculations (see later for details). Energies for OH transfer from phenol to the ortho, meta, and para positions in anisole were negligible (0.0, 0.0, and 0.1 kcal mol^{-1}).

Since the above ideas suggest that the *o*-hydroxy effect is not due to a destabilizing interaction in the guaiacol molecule, it must arise from a stabilizing effect in the product *o*-hydroxyphenoxy radical. The most obvious origin of this stability is a hydrogen bond in the radical which is >4.7 kcal stronger than in the molecule. As discussed later, a closely related H bond of this nature was discussed by Linstead and co-workers[37] in their analysis of H transfer to quinones.



(5)

C. Phenetole and *o*-Hydroxyphenetole. Additional confirmation for the large *o*-hydroxy effect is provided by decomposition rate studies of phenetole and *o*-hydroxyphenetole. Their unimolecular rate constants and RRKM fits to the experimental rate data are shown in Figure 3.

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(29) This insensitivity of extrapolated VLPP data to the magnitude of the Arrhenius parameters has been discussed in our earlier studies of ethylbenzene.[24] It is due to the different degrees of falloff predicted by different sets of Arrhenius parameters.

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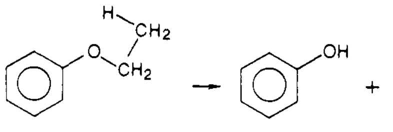
Very low pressure pyrolysis studies of phenetole have previously been carried out by Colussi et al.[25] They concluded that the reaction proceeds by homolysis. Their rate constants, included in Figure 3, are about 15% lower than ours. Considering possible uncertainties in temperatures and reactor collision numbers,[19] we regard this as good agreement. Our high-pressure rate constants were fit to the equation $k_1 = 10^{15.5} \exp(-E_a/RT)$, with E_a equal to 61.9 kcal mol^{-1} for phenetole and 55.2 kcal mol^{-1} for *o*-hydroxyphenetole. Therefore, *o*-hydroxy substitution in phenetole lowers the O–ethyl bond strength by 6.7 kcal mol^{-1}, comparable to the bond weakening caused by this substituent in anisole.

D. Methoxyanisoles. Relative BDEs for methoxyanisoles are included in Table III. The influence of a methoxy substituent on anisole is quite different than that of a hydroxy substituent. In both the ortho and para positions it caused a sizable 4 kcal mol^{-1} bond weakening. This is in sharp contrast to the nearly 5 kcal mol^{-1} difference between *o*- and *p*-hydroxyl substituents.

E. Other Reaction Mechanisms. (i) Concerted versus Homolytic Reaction. The following observations show the absence of concerted reactions leading to alkane formation from *o*-hydroxyanisole and -phenetole: (1) methyl radical/methane peak intensity ratios were the same for all anisoles, (2) in the decomposition of *o*-hydroxyphenetole little ethane was formed (the data in Table IV suggests a possible small contribution from the concerted reaction of perhaps 5% in the *o*-hydroxyphenetole reaction), and (3) the yield of methane per decomposed guaiacol molecule was low (ca. 17%) and comparable to that formed in the decomposition of *m*-hydroxyanisole.

Recently, Vuori[1] measured the total stable spin concentration in the products of liquid-phase pyrolysis of hydroxyanisoles. On the basis of these measurements of the products of *o*- and *p*-hydroxyanisole pyrolysis, he qualitatively concluded that the concerted mechanism was not the main reaction pathway in the thermal decomposition of guaiacol. Our experiments suggest that this path is negligible.

For the phenetoles, there is the possibility of a 4- or 6-centered concerted elimination pathway (reaction 6 and 7) also leading to the observed ethylene product. Evidence for such processes leading to a phenoxyl radical has been given by Daly and co-workers[38] for *tert*-butyl phenyl ether. Colussi et al.,[25] however, concluded that phenyl ethyl ether decomposed by homolysis. Also, Gilbert and Gajewski[40] did not find evidence for the concerted reaction path in the thermal decomposition of phenethyl phenyl ether.



(6)

(7)

In any event, the effect of *o*-hydroxyl would be expected to be small, possibly even inhibitory, on such concerted reactions. Hence, the observed rate enhancement cannot be explained in terms of these reactions. The similarity of *o*-hydroxyl effects on rates of decomposition of anisole and phenetole suggests that the principal dissociation pathways are the same (that is, homolysis). However, the present results do not rule out a sizable contribution from a concerted reactions in the case of phenetole.

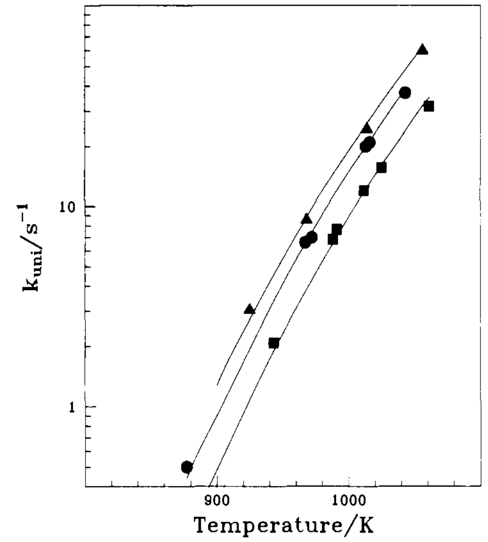


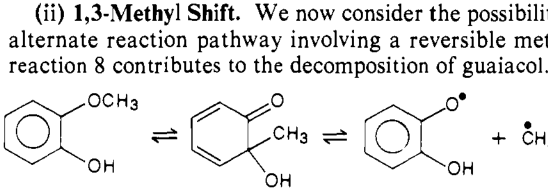
Figure 4. Rate constants measured from the thermal decomposition of the three isomeric methoxyanisoles; (▲) ortho, (■) meta, (●) para. The solid lines are the RRKM fits to the data.

Table VI. Calculated (AM1) Differences in Energies of Substitution in Anisoles and Phenoxy Radicals[a]

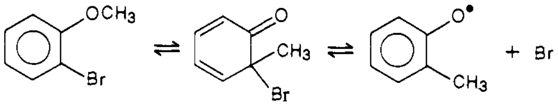
	substituent position					
	ortho		meta		para	
substituent	molec	r	molec	r	molec	r
OH	0.1	−5.9	−0.4	0.2	0.6	−3.4
OCH_3	3.4[b]	−1.9[b]	−0.4	−0.3	0.6	−3.5
Cl	4.2	3.3	0.4	1.4	0.0	0.5
Br	4.0	3.4	0.4	1.1	−0.1	0.8

[a] A positive sign indicates destabilization (relative to benzene) induced by attachment of the substituent. [b] Values for the more stable trans isomer.

(ii) 1,3-Methyl Shift. We now consider the possibility that an alternate reaction pathway involving a reversible methyl shift, reaction 8 contributes to the decomposition of guaiacol. In order to test for the occurrence of this pathway, we determined the rate of decomposition of *o*-bromoanisole (Figure 1). If this mechanism were significant, then, since C–Br bonds are about 18 kcal mol^{-1} weaker than C–CH$_3$ bonds,[41] *o*-bromoanisole dissociation according to eq 9 would be several orders of magnitude faster than that of anisole. However, *o*-bromoanisole decomposed only a factor of 2 faster than anisole. Moreover, in separate studies, *o*-chloroanisole was found to decompose at nearly the same rates as *o*-bromoanisole (Figure 1), suggesting that even this modest rate increase is due simply to an ortho proximity effect.



(8)



(9)

We also note that an irreversible methyl shift can also be excluded because it would have a tighter transition state (lower *A* factor) than simple homolysis and, in cases where the same products are generated, it would have at least as high an activation barrier.

On the basis of above mechanistic studies, we conclude that the unimolecular decomposition of all anisoles occurs by single-step O–methyl bond homolysis.

F. Theoretical Calculations. In an effort to separate net substituent effects arising from effects on the molecule from those due to effects on the radical, we calculated heats of formation of a number of substituted anisoles and substituted phenoxy radicals by the AM1 method.[42] We also hoped that it might also provide insight into the observed *o*-hydroxy effect. AM1 is an improved version of the widely used MNDO method. It has been

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Table VII. Comparison of Rate Constants ($k_1^\infty \times 10^5$ s^{-1}) at 648 K for the Thermal Decomposition of Substituted Anisoles

		condensed phase		
			neat	
compound	gas phase[a]	in tetralin[b]	b	c
anisole	0.15	0.35	0.78	0.58
guaiacol	37.0	43.3	37.3	14.5
3-hydroxyanisole	0.12	0.39	2.95	
4-hydroxyanisole	1.10	3.09	4.94	
2-methoxyanisole	7.30	7.84	8.68	
3-methoxyanisole	0.66	0.96	1.67	
4-methoxyanisole	6.30	4.94	5.89	

[a] Extrapolation of present rate constants to 648 K. [b] Reference 1. [c] Reference 6.

shown to reasonably account for hydrogen bonding.[42] Details of the optimization procedure are described elsewhere.[43]

AM1 heats of formation of substituted anisoles and related phenoxyl radicals are shown, relative to substituted benzenes, in Table VI. For para substitution, almost all of the substituent effect stems from its influence on the radical, rather than the molecule. For meta substitution, effects are small and of comparable magnitude in the radical and molecule. For ortho substituents, effects on the molecule can be significant.

As mentioned above, guaiacol is predicted to have no net substituent–substituent interaction in the molecule so that any bond weakening is predicted to be due entirely to the effect of the substituent in the radical. In contrast, for *o*-methoxyanisole, relief of substituent interference in the molecule is predicted to be the major contributor to the bond weakening. However, an experimental measurement of the heat of formation of this compound shows no destabilization,[35] casting some doubt on the accuracy of the calculated values.

While on the average AM1 calculations are in good agreement with observed ΔBDE (±1 kcal mol^{-1}, Table III), the most interesting effects are not predicted. Specifically, contrary to experiment, AM1 calculations imply that the effects on ΔBDE of hydroxy and methoxy substituents are nearly the same. Also, the very large *o*-hydroxy effect is not predicted. The substituent effects observed here, while large in terms of free-radical stability, are apparently within the error limits of AM1.

G. Comparison with Condensed-Phase Results. Liquid-phase thermolysis studies by Vuori,[1] Bredenberg,[2-4] Virk,[6] and their co-workers show that the decomposition rates of hydroxy- and methoxy-substituted anisoles depend strongly on the position of substitution. With use of our gas-phase Arrhenius parameters, rate constants for the decomposition of anisole, the hydroxyanisoles, and the methoxyanisoles are compared with these condensed-phase results in Table VII.

Overall, gas- and condensed-phase rate constants, particularly the condensed-phase values of tetralin (1,2,3,4-tetrahydronaphthalene) determined by Vuori et al.,[1] are remarkably close, considering the substantial temperature extrapolation involved and the possibility of radical-induced reactions in the condensed-phase studies. This immediately indicates that, in the condensed-phase reactions, long-chain processes do not occur and a large fraction of this decomposition proceeds by simple homolysis. Reaction rates of guaiacol and the methoxyanisoles are in especially good agreement. For the others, namely anisole, and 3- and 4-hydroxyanisole, condensed-phase values are 2–4 times faster. Note that these are less reactive compounds. It may be that the more severe conditions required for their study caused an increase in the participation of alternative decomposition processes.

H. Substituent Effects on Phenoxy Radicals. Substituent effects on O–H bond strengths in phenols have recently been reviewed by Densiov and Khudyakov.[44] Recent and relatively direct determinations are those of Mahoney and DaRooge,[11] where values were derived from equilibrium constants based on measurements of forward and reverse rate constants for H-transfer reactions. Values were also reported that used a single H-transfer rate constant assuming the Brøsted relationship ($K_{eq} \propto k_{rate}$). The latter method assumes the absence of "polar effects" and was shown to hold for a number of substituents. The other determinations of substituent effects reviewed by Denisov and Khudyakov are in general agreement with those from ref 11. Very recent determinations by photoacoustic methods have been reported by Mulder et al.[45] for four para substituents (CF_3, Cl, *t*-Bu, and CH_3O).

Before comparing the present results for O–CH_3 bonds in anisoles with those of O–H bonds in phenols of Mahoney and DaRooge and Mulder, we will show that for the substituents of interest ΔBDE for these two bonds should be nearly the same.

Differences in ΔBDE for these two bonds are equal to the enthalpy of substituent "disproportionation" as follows:

$$\Delta\mathrm{BDE}(\mathrm{XPhOCH_3}) - \Delta\mathrm{BDE}(\mathrm{XPhOH}) = \Delta H(\mathrm{PhOH} + \mathrm{XPhOCH_3} = \mathrm{XPhOH} + \mathrm{PhOCH_3}) \quad (10)$$

Since the O–H and O–CH_3 bonds are isolated from both the substituent X and the aromatic system, this reaction enthalpy is expected to be quite small. As discussed earlier, even for cases where there are significant differences in substituents (OH versus H, for instance), these disproportionation energies are not large.[32-35] Theoretical results in the literature[36] support this idea. Therefore, we expect to make little error when equating differences in O–CH_3 bond strengths in anisoles with differences in O–H bond strengths in phenols.

Mahoney and DaRooge's values of relative O–H BDEs in *m*- and *p*-hydroxyphenols and *p*-methoxyphenol are included in the Table III. For the value obtained from their equilibrium measurement (*p*-methoxy), the two methods are in excellent agreement.[11] However, ΔBDEs for *m*-hydroxyphenol and *p*-hydroxyphenol obtained by the Brøsted method are substantially different than ours. We believe that this difference is likely due to polar effects in the H-transfer reactions and the resulting inapplicability of the Brøsted approximation used by Mahoney and DaRooge in estimating bond strengths. We suggest that the close relationship between reaction thermodynamics and H-abstraction kinetics reported by them held only because it was applied only to relatively nonpolar substituents (*tert*-butyl, phenyl, methyl, methoxy, etc.).

Measured rates of H transfer from *o*-hydroxy phenols are at best only slightly faster than from *p*-hydroxyphenols[46,47] despite a 5 kcal mol^{-1} weaker O–H bond strength. Apparently, the extra stabilization caused by the *o*-hydroxy group is not developed in the transition state for abstraction.

The very recent measurements of Mulder et al.[45] indicate a stabilization by the *p*-methoxy substituent that is 1.9 kcal larger than the present values (and 1.6 kcal larger than Mahoney and DaRooge's measurements). These differences could conceivably originate from differences in bond dissociation entropies, since the present dissociation rates (and Mahoney's equilibrium constants) would be sensitive to these effects (for simplicity, assumed to be negligible in the present analysis), while the direct heat release measurements of Mulder et al.[45] are sensitive only to energies. In this case, approximately $^1/_3$ of the 5.9 kcal enthalpy effect measured by the latter workers is compensated for by entropy in the net effect on Gibbs bond energies near room temperature.

I. Reactivity of *o*- and *p*-Quinones. The present results suggest that an important reason for the general observation that *o*-quinones are more reactive than *p*-quinones[30] is the more favorable thermochemistry for H-atom transfer to the ortho isomer; Linstead and co-workers[37] reported that Gibbs energies for H transfer from 1,4-dihydronaphthalene to 1,2-naphthoquinone was 5 kcal lower than transfer to 1,4-naphthoquinone. This value is

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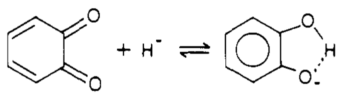

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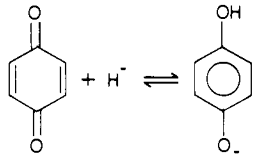

(12)

of the same magnitude as the present measured difference in stabilization energies of *o*- and *p*-hydroxyphenoxy radicals (4.6 kcal). Linstead explained these differences in reactivity in terms of intramolecular H bonding in the species generated by H addition to the *o*-quinones. Linstead, however, argued that anionic intermediates are involved. In this case, one might conclude that *o*-hydroxyphenoxy stabilization energies are of the same magnitude in anions and free radicals. On the other hand, the actual mechanism of H transfer to quinones is not well established.[37]

V. Summary

(1) The primary decomposition step in all dissociation reactions of anisoles is O–methyl bond homolysis. The decomposition rate is very sensitive to the nature and position of the substituent.

(2) The *o*-hydroxy substituent has large effect, weakening the phenoxy–CH_3 and phenoxy–CH_2CH_3 bonds by about 7 kcal mol^{-1}. The presence of a strong hydrogen bond in the radical seems to be the best explanation for this effect.

(3) Relative dissociation rates of anisole, *o*-bromoanisole, and *o*-chloroanisole show that a 1,3-methyl shift is not a significant reaction pathway in their decomposition reactions.

(4) Rate parameters from the present experiments reproduce rates of decomposition in condensed-phase thermolysis reactions. This suggests that even in the complex reaction environments of lignin and coal thermolysis simple bond homolysis is an important, perhaps rate-controlling, step in the decomposition of alkyl aryl ethers.

(5) A comparison of the present bond strengths and H-abstraction rate constants from phenols suggests that substantial polar effects are operative in the H-abstraction reactions.

(6) In agreement with Linstead et al.,[37] the present results suggest that the higher reactivity of *o*-quinones than *p*-quinones may be largely due to the exceptional stability of the *o*-hydroxyphenoxy radical (or anion) formed by H transfer to the former molecules.

Acknowledgment. This work was supported by a grant from the Gas Research Institute.

Registry No. *o*-Bromoanisole, 578-57-4; *o*-chloroanisole, 766-51-8; *o*-hydroxyanisole, 90-05-1; *m*-hydroxyanisole, 150-19-6; *p*-hydroxyanisole, 150-76-5; phenetole, 103-73-1; *o*-hydroxyphenetole, 94-71-3; *m*-methoxyanisole, 151-10-0; anisole, 100-66-3; *m*-chloroanisole, 2845-89-8; *p*-chloroanisole, 623-12-1; *m*-bromoanisole, 2398-37-0; *p*-bromoanisole, 104-92-7; *o*-hydroxyphenoxy radical, 5593-75-9; *o*-methoxyphenoxy radical, 41115-74-6; *o*-chlorophenoxy radical, 63125-12-2; *o*-bromophenoxy radical, 63125-15-5; *m*-hydroxyphenoxy radical, 24856-47-1; *m*-methoxyphenoxy radical, 28504-31-6; *m*-chlorophenoxy radical, 54560-44-0; *m*-bromophenoxy radical, 63125-14-4; *p*-hydroxyphenoxy radical, 3225-30-7; *p*-methoxyphenoxy radical, 6119-32-0; *p*-chlorophenoxy radical, 3148-13-8; *p*-bromophenoxy radical, 63125-13-3; *p*-methoxyanisole, 150-78-7; *o*-methoxyanisole, 91-16-7.

Carbanionic Rearrangements of (Halomethylene)cycloalkanes

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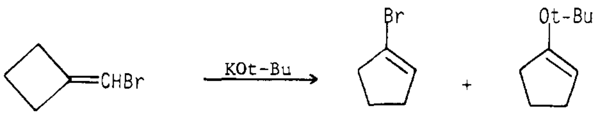
Abstract: The mechanism for the unusual base-induced ring-enlargement reaction of (halomethylene)cyclobutanes to 1-halocyclopentenes was examined by C-13 labeling studies with (bromomethylene)cyclobutane (**1**), *cis*- and *trans*-1-(bromomethylene)-3-ethoxy-2,2-dimethylcyclobutane (**15** and **16**), and 1-(bromomethylene)-2,2,4,4-tetramethylcyclobutane (**22**). Two competing processes were found to lead from the vinyl anion to rearranged products: (1) rehybridization of the vinyl anion to a 1,2-carbene–anion, which subsequently undergoes rearrangement, and (2) a Beckmann-like simultaneous migration of bromide and ring carbon. Both processes subtly bypass the "forbidden" alkyl-to-carbanion shift.

In 1968 the unusual rearrangement reaction of (bromomethylene)cyclobutane (**1**) to 1-bromocyclopentene (**2**) in the presence of potassium *tert*-butoxide was reported (eq 1).[1] The rearranged bromide was accompanied by small amounts (2–4%) of the ring-enlarged enol ether 1-*tert*-butoxycyclopentene (**3**). It was shown that **3** arises from carbene and cyclopentyne intermediates, in analogy to larger ring homologues,[2] but 1-bromocyclopentene (**2**) does not. Thus, Diels–Alder trapping of the cyclopentyne intermediate has no effect on the yield of **2** while that of **3** drops to zero (Scheme I).[1,3]



1 **2** **3**

(1)

Evidence for the intermediacy of cyclopentyne in ring enlargements of methylenecycloalkanes generated from (diazomethylene)cyclobutanes[4] and (dibromomethylene)cyclobutanes[5] has also been reported, so the rearrangement of **1** to **3** cannot be considered unusual. However, the rearrangement of **1** to **2** is totally unexpected and mechanistically of great interest.

Several mechanisms for the **1** to **2** conversion may be written and are depicted in Scheme II. All involve the vinyl carbanion **4**, whose presence in the reaction medium has been amply demonstrated by deuterium-exchange studies.[3,6] The above-cited trapping experiments and stereochemical studies[7] (vide infra) have

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