

Comparative Study of Anisole and 4-Vinylanisole Pyrolysis: Insight into Char, Tar, and Particle Formation During Lignin Pyrolysis

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Lignin pyrolysis generates oxygenated aromatics that can serve as renewable biofuel precursors. Anisole and substituted anisoles are widely used as model compounds to probe processes related to their production and use. We present a comparative study of anisole and 4-vinylanisole thermal decomposition using vacuum-ultraviolet photoionization mass spectrometry in a silicon carbide microreactor from 300 to 1300 K. For both molecular species, the initial decomposition pathway is O—CH₃ bond cleavage. The vinyl substituent lowers the bond dissociation energy, shifting decomposition to lower temperatures for 4-vinylanisole. Anisole pyrolysis produces hydrogen-atom, methyl, propargyl, phenoxy, and cyclopentadienyl radicals, phenol, cyclopentadiene, cyclopentadienyl dimer, methylcyclopentadiene, CO, acetylene, and benzene via methylcyclopentadiene. The products of 4-vinylanisole pyrolysis include hydrogen-atom, methyl, propargyl, fulvenallenyl, vinylphenoxy, vinylcyclopentadienyl, and cyclopentadienyl radicals, vinylphenol, vinylcyclopentadiene, dimethylfulvene, fulvenallene, vinylacetylene, CO, and acetylene, but no benzene. Vinyl substitution thus facilitates resonance-stabilized radical (RSR) formation at temperatures lower than the cracking temperature of anisole. Whereas 4-vinylanisole decomposes at a lower temperature than anisole, both species produce significant RSR products that facilitate aromatic growth and gas-to-condensed-phase hydrocarbon conversion, in contrast to their methyl-substituted analog. These new insights into RSR formation are applicable to lignin pyrolysis and may be useful for limiting char or tar formation during biofuel production and for developing predictive models of emissions from smoldering and propagating flaming wildfires.

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I. INTRODUCTION

Biomass is becoming an important and renewable source of sustainable fuels and chemicals, providing alternatives to fossil fuels and petrochemicals. Pyrolysis of biomass generates a complex mixture of oxygenated compounds; these pyrolysis products can be used as biofuels, the compositions of which are determined by the type of biomass pyrolyzed [1–3]. The products of biomass pyrolysis also contribute significantly to wildfire emissions [4–7].

Biomass primarily consists of cellulose, hemicellulose, and lignin. Cellulose and hemicellulose are saccharide polymers, largely composed of interconnected substituted oxanes. Lignin, the second most abundant biomass component, is an aromatic polymer of phenolic and methoxy groups [8–12]. Lignin is composed of three base structural units, *p*-hydroxyphenyl, guaiacyl, and syringyl, the structures for which are shown in Fig. 1(a) [13,14]. Pyrolysis of lignin produces species derived from these structural units, including anisole and substituted anisoles [15,16], structures for which are shown in Fig. 1(b). These oxygenated species are promising for use as bioderived fuels. They are also emitted during wildfires, and their chemistry is relevant to wildfire gas and particle-phase emissions. Understanding the pyrolysis chemistry of these products is important for tailoring lignin pyrolysis processes to the production of bioderived fuels and other products and for predicting emissions from flaming and smoldering combustion during wildfires [6].

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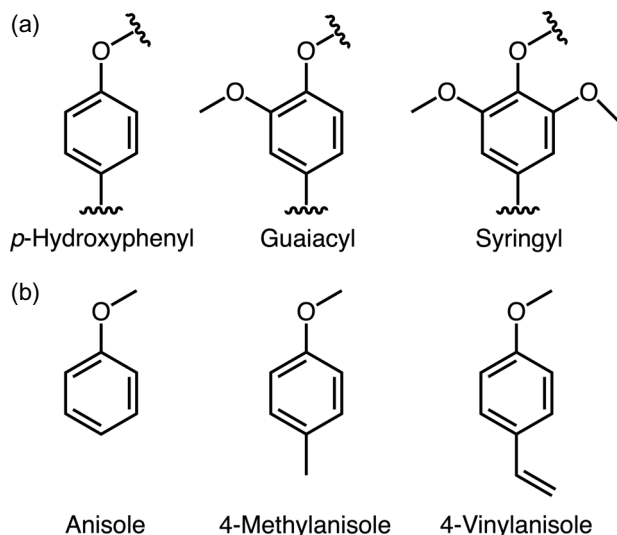


FIG. 1. Structures of lignin base units, anisole, and substituted anisoles. Structures are shown for (a) the lignin base units, *p*-hydroxyphenyl, guaiacyl, and syringyl, and (b) selected products of lignin pyrolysis, anisole, 4-methylanisole, and 4-vinylanisole.

Anisole and substituted anisoles are some of the simplest model compounds for investigating the pyrolysis chemistry of lignin [6,17,18]. Anisole has been studied extensively to gain insight into its pyrolysis and combustion behavior. Studies have focused on its laminar flame speed [18–21], ignition delay times [22,23], thermal decomposition kinetics, chemical mechanisms, and product formation [6,17,18,21,24–43]. These studies have facilitated kinetic model development and insight into anisole-decomposition chemistry.

Many studies have shown that the breaking of the O—CH₃ bond is the primary decomposition pathway for anisole [17,18,21,27,32,35,36,40,42,44–47]. This unimolecular decomposition pathway inhibits radical propagation because the resonance-stabilized phenoxy radical, thereby formed, consumes H atoms to produce the stable closed-shell species phenol and cyclopentadiene after the loss of CO. Friderichsen *et al.* [17] and Scheer *et al.* [40] studied anisole pyrolysis using vacuum-ultraviolet (VUV) photoionization mass spectrometry (PIMS). Friderichsen *et al.* [17] used infrared spectroscopy, and Scheer *et al.* [40] used resonance-enhanced multiphoton ionization (REMPI) to identify isomers. They concluded that benzene is primarily formed via methylcyclopentadiene decomposition and that naphthalene is produced via cyclopentadienyl dimerization. Li *et al.* [46,47] used a similar reactor and VUV PIMS and similarly concluded that benzene is generated via methylcyclopentadiene formation and decomposition. Kaiser *et al.* [48] reproduced the experiments of Friderichsen *et al.* [17] and Scheer *et al.* [40] and confirmed their results using an identical reactor, VUV

PIMS, and VUV photoionization efficiency (PIE) curves to identify products. Carpenter *et al.* [49] reanalyzed the data from Scheer *et al.* [40] and concluded that propargyl dimerization was competing with methylcyclopentadiene decomposition to produce benzene in those experiments.

Previous experimental work by Mulcahy and Williams [50], Mackie *et al.* [42], and Pecullan *et al.* [36] showed that the phenoxy and methyl products of the initial bond cleavage can recombine to form methylcyclohexadienones, which can then rearrange to form *o*- and *p*-cresol, all of which are isomers of anisole. These experimental results are supported by the theoretical work of Pratali Maffei *et al.* [43]. Their calculations show that, at higher temperatures, anisole decomposition can lead to methylcyclopentadiene and CO formation via the reaction of cyclopentadiene and methyl, supporting experimental results [40,46–48]. Carpenter *et al.* [49] suggested that either methylcyclohexadienones or cresols could lose an H atom to yield methylphenoxy, which can further fragment, losing CO, to form methylcyclopentadiene.

Nowakowska *et al.* [34] performed experimental studies of anisole pyrolysis and oxidation using a jet-stirred reactor, combined with detailed kinetic modeling; they concluded that the decomposition of anisole is a first-order reaction that is not influenced by the presence of oxygen. The primary products are phenoxy radicals and phenols, which further decompose into cyclopentadienyl radical and cyclopentadiene. The subsequent radical chemistry involving cyclopentadienyl radical leads to aromatic formation at relatively low temperatures (e.g., 1000 K) with little or no involvement from the hydrogen-abstraction-C₂H₂-addition (HACA) mechanism, the primary mechanism typically invoked to explain molecular-weight growth during rich hydrocarbon combustion [51,52]. Work by Yuan *et al.* [27] on anisole pyrolysis and by Bierkandt *et al.* [33] on anisole combustion in fuel-rich premixed flames confirmed the results of Nowakowska *et al.* [34]. These conclusions are supported by the results of Sood *et al.* [25], who demonstrated that the addition of anisole to rich premixed flames strongly enhances both oxygenated and non-oxygenated aromatics, and those of Zhang *et al.* [35], who reported benzene formation at 400 °C and toluene formation at 450 °C during anisole pyrolysis.

Substituted anisoles are good surrogates for lignin-based biofuels and valuable for gaining insight into the pyrolytic behavior of biomass [24,53,54]. The simplest substitution involves the addition of a methyl group or a vinyl group to anisole. There have been a few studies on the pyrolysis of 4-methylanisole (4-MA). Sood *et al.* [24] found that although the structure of 4-MA is similar to that of anisole, as is the initial decomposition via the cleavage of the O—CH₃ bond, the subsequent decomposition differs significantly. The addition of a methyl group to anisole has an impact on the formation of small polycyclic aromatic hydrocarbons (PAHs) but has little effect on the larger

PAHs once the precursors are formed. For comparison, anisole pyrolysis leads to the formation of benzene and naphthalene as the primary PAHs, whereas 4-MA leads to methyl-substituted phenols, supporting hypothesized mechanisms involving growth via toluene and phenol.

The results of theoretical studies using density functional theory (DFT) suggest that the methyl substitution at the para position (4-MA) on the benzene ring lowers the O—CH₃ bond dissociation energy (BDE) by approximately 1.5–2 kcal/mol [6,7,47]. Coupled experimental and theoretical work of Suryan *et al.* [55] showed that pyrolysis temperatures and O—CH₃ BDEs are lower for para- and ortho-substitutions than for the meta-substitution. Experimental and theoretical work by Li *et al.* [46,47] supported these conclusions, as have other theoretical results [6,7]. Suryan *et al.* [55] also showed that electron-withdrawing groups in the para position strengthen the O—CH₃ bond, whereas electron-withdrawing groups in the ortho position weaken it. Theoretical studies have generally suggested that electron-donating-group substitutions on the benzene ring and resonance stabilization of the substituted phenoxy-radical product both decrease the O—CH₃ BDE relative to that of unsubstituted anisole. Electron-withdrawing-group substitutions have the opposite effect [56–58].

Vinyl-substituted products of lignin pyrolysis are of particular interest with respect to tar or char formation. Alkenyl groups, which predominantly occur as vinyl groups [16], are typically formed by dehydration reactions during lignin pyrolysis and are more reactive than methoxy groups [8]. The β -O-4 bond is the primary linkage in lignin. Homolytic cleavage of the C β —O bond of the β -O-4 linkage during pyrolysis occurs at relatively low temperatures (300 °C) to yield vinyl-substituted products, such as 4-vinyanisole, after dehydration [59–62]. Figure 2 shows a proposed mechanism for 4-vinyanisole production from a lignin *p*-hydroxyphenyl dimer via homolytic cleavage of C—C and C—O bonds of linkages between the lignin monomers. Yin *et al.* [62] proposed this mechanism for the production of 4-acetylanisole and phenol, both of which they observed during pyrolysis of a model lignin polymer of *p*-hydroxyphenyl with β -O-4 linkages. Calculations by Chen *et al.* [60] predicted that 4-vinyanisole will further pyrolyze to form the 4-vinylphenoxy radical and 4-vinylphenol (also known as 4-hydroxystyrene), the latter of which was observed by Yin *et al.* [62] during pyrolysis of a model lignin polymer of *p*-hydroxyphenyl and is typically a major product of the pyrolysis of herbaceous lignin [63,64].

In addition to being a product of lignin pyrolysis, 4-vinyanisole (also known as 4-methoxystyrene and *p*-vinyanisole) is a well-known natural product [65]. It is an aggregate pheromone for locusts [66–68] and an attractant for some pollinators [69,70], a prominent component of a large variety of brandies [71,72] and

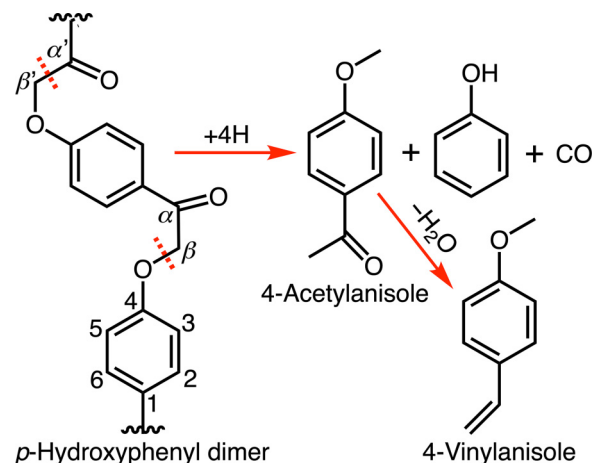


FIG. 2. The proposed mechanism for the production of 4-vinyanisole (also known as 4-methoxystyrene) from lignin pyrolysis. Cleavage of the C α' —C β' bond and the C β —O bond of the β -O-4 linkage in lignin yields CO, phenol, and 4-acetylanisole (also known as 4-methoxyacetophenone), the latter of which is converted to 4-vinyanisole via dehydration.

pharmaceutically interesting essential oils [73–75], and a contributor to the fragrances of selected philodendrons [69] and roses [76–78], imbuing the scent of the Diana tea rose, for example, with “freshness and diffusiveness” [77]. It is also commercially valuable as a precursor in the synthesis of substituted polystyrene [79,80] and has been used in the synthesis of solid polymer electrolytes for lithium-ion batteries [81].

The chemistry of 4-vinyanisole, however, has been the subject of few investigations. Hendricker *et al.* [82] performed pyrolysis-membrane-inlet mass spectrometry on 4-vinyanisole pyrolyzed at atmospheric pressure at a temperature of 450 °C. The 4-vinyanisole was pyrolyzed with the methylating agent tetramethylammonium hydroxide (TMAH). The TMAH appeared to have little effect on the mass spectrum, except for yielding a significant peak at the parent mass of TMAH of 91 Da. The other major peaks included the 4-vinyanisole parent peak at 134 Da and pyrolysis products at 119 and 65 Da. Because the authors were looking for a protonation product at 135 Da, which did not appear, they did not analyze the mass spectrum further.

Jin *et al.* [83] pyrolyzed 4-vinyanisole to produce a peak at m/z 91, which they identified via tunable VUV photoionization as vinylcyclopentadienyl radical with an ionization energy of 7.84 eV. McClish *et al.* [84] similarly pyrolyzed 3-vinyanisole to form the product at m/z 91 and recorded its mass-selected threshold photoelectron spectrum, which they analyzed using high-level *ab initio* coupled-cluster calculations. The spectrum revealed two distinct states, which were unambiguously assigned to ionization into the singlet ground state of the vinylcyclopentadienyl cation at

7.81 ± 0.02 eV and ionization into its first triplet state at 8.08 ± 0.02 eV. Previous theoretical results by Savee *et al.* [85] suggested energies of 7.94 eV for transition to the lowest singlet cation state and 8.13 eV for transition to the lowest triplet cation state.

Previous theoretical studies have indicated that electron-donating-group substitutions in the para position on the benzene ring decrease the O—CH₃ BDE relative to the unsubstituted anisole [56–58]. The vinyl group is electron donating, and 4-vinylanisole would thus be expected to have a weaker O—CH₃ bond than anisole. Suryan *et al.* [55] used low-pressure pyrolysis of ortho-substituted anisoles with product detection by mass spectrometry and showed that vinyl substitution in the ortho position on the benzene ring weakens the O—CH₃ bond by approximately the same amount as ortho-methyl substitution does. Their semiempirical molecular-orbital calculations suggested, however, that the vinyl substituent should weaken the O—CH₃ bond significantly more than the methyl substituent. They speculated that removal of the methyl from the methoxy group provides steric relief with the vinyl substituent in the ortho position. In addition, the vinyl group more significantly extends the conjugation of the resonance-stabilized radical (RSR) phenoxy product. The steric effect is irrelevant for the para position, but vinyl substitution would still be expected to lower the O—CH₃ BDE relative to methyl substitution based on extended conjugation of the RSR product.

In a study of methyl-substituted anisoles, Sood *et al.* [24] suggested that 4-vinylanisole is formed from 4-methylphenoxy through a series of reactions involving methyl addition and hydrogen loss. They further postulated that 4-vinylanisole readily undergoes ring closure to produce benzofuran.

We present a comparative study of the pyrolysis of 4-vinylanisole and anisole. We used vacuum-ultraviolet (VUV) photoionization mass spectrometry to detect products of 4-vinylanisole and anisole pyrolyzed at temperatures of 300–1300 K in a silicon carbide microreactor. The experiments were performed on Beamline 9 at the Advanced Light Source, which supplied tunable photon energies and allowed for isomer identification and distinction between photoionization fragmentation and pyrolytic decomposition. Our results demonstrate that both species produce a range of RSRs frequently associated with high-temperature gas-to-condensed-phase hydrocarbon conversion. Differences include the production of benzene by anisole and the formation of substantial fulvenallene and 4-vinylphenol by 4-vinylanisole. Such significant RSR-product formation has not been observed for 4-methylanisole, perhaps explaining the enhanced char-tar formation of alkenyl-substituted lignin pyrolysis products over alkyl-substituted products. Significant RSR formation may also facilitate particle formation during wildfires.

II. METHODS

All experiments were performed at Beamline 9.0.2 of the Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory (LBNL). This beamline provides a high flux of tunable VUV photons, generated by an undulator and monochromator system [86,87]. For these experiments, we employed photons of energies between 7.7 and 11.0 eV to ionize hydrocarbon species, including aromatic and radical intermediates, while minimizing fragmentation. The tunability of the VUV source enables photoionization efficiency (PIE) measurements, which facilitate the identification of closed-shell and radical species.

Figure 3 provides a schematic diagram of the experimental setup. The thermal decomposition chemistry was investigated using a silicon carbide (SiC) microreactor [88–92], which provides a confined reaction environment with rapid and uniform heating characteristics. The microreactor is 38 mm long, has an inner diameter of 1 mm and an outer diameter of 2 mm, and has a 100- μ m aperture just upstream of its inlet. It is resistively heated by applying current through molybdenum clips to carbon electrodes on the ends of the reactor, enabling stable operation over a wide temperature range. The temperature is measured with a Type C thermocouple attached to the outside surface of the reactor. The heated region between the electrodes is approximately 14 mm.

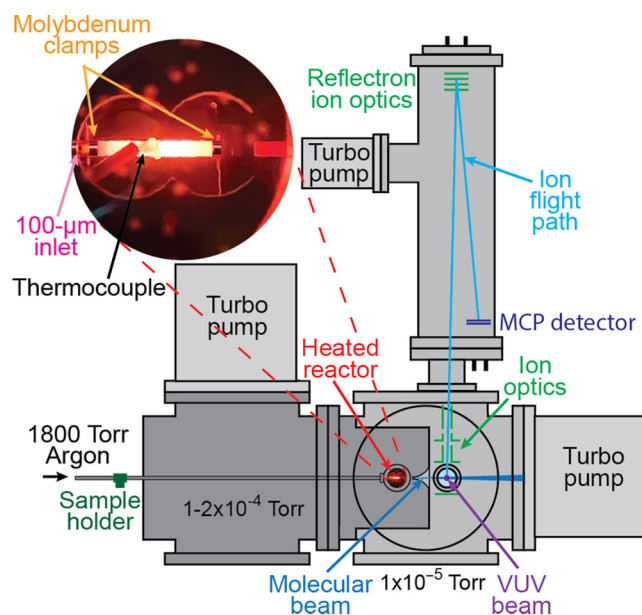


FIG. 3. A schematic diagram of the experimental setup. The experiment was performed using a reflectron time-of-flight mass spectrometer. The sample was seeded in argon and pyrolyzed in a heated silicon carbide reactor. The products were cooled in a molecular beam and ionized using tunable VUV photoionization.

The reactor temperatures were varied from 300 to 1300 K in 50-K increments. These temperatures were sufficient to induce unimolecular decomposition of the parent species. The step size provided adequate resolution to track the onset and progression of decomposition with temperature. Once steady state was achieved, the temperature fluctuations did not exceed 2 K.

The compact geometry of the reactor minimizes residence times, thereby reducing the influence of secondary chemistry [88,91]. The flow rate and residence time in the microreactor are difficult to determine. We estimate the flow rate into the microreactor through the 100- μm orifice to be approximately 175 sccm, given an upstream pressure of 1800 Torr and a downstream pressure of 1×10^{-4} Torr [93]. Based on previous studies [88–92], we estimate our residence time in the hot region of the reactor to be in the range of 30–80 μs .

The target species studied were anisole and 4-vinylnisole, which were introduced into the gas stream by passing argon through the liquid-sample reservoir. A backing pressure of 1800 Torr (35 psia) was applied to the argon carrier gas, producing a stable supersonic expansion through the reactor outlet into the vacuum chamber. The sample was diluted in argon to suppress bimolecular chemistry and clustering effects, isolate unimolecular decomposition pathways, and simplify the comparison between anisole and 4-vinylnisole decomposition chemistry. To increase the vapor pressure and reactor concentration of 4-vinylnisole, which is less volatile than anisole, we heated the sample holder to a temperature of 340 K. This temperature was held constant throughout the experiment.

A molecular beam was created by skimming the expansion outside the reactor, and molecular species were cooled via free-jet expansion [94–97]. Operating the reactor outlet under choked-flow conditions ensures a well-defined constant mass flow rate that is independent of downstream pressure fluctuations. This steady-flow condition provides stable and reproducible reactor conditions [88,91,97,98]. In addition, the supersonic free-jet expansion that follows the nozzle exit produces extremely rapid adiabatic cooling (on the order of microseconds) and reduced collision frequency, which effectively “freezes” the high-temperature chemical composition generated in the reactor by quenching further reactions, fragmentation, and secondary chemistry prior to photoionization. Reactive intermediates and primary pyrolysis products can thus be sampled with minimal post-reactor evolution.

Reaction products were detected using VUV photoionization mass spectrometry (PIMS) with a reflectron time-of-flight (TOF) mass analyzer (R. M. Jordan Co., c. 2002). Further details about the mass spectrometer and its operation can be found in Golan and Ahmed [99]. The TOF system provides high mass resolution and rapid acquisition rates for tracking the temporal and thermal evolution

of transient intermediates. Each mass spectrum shown here represents an average of 200 000 sweeps with a sampling rate of 5 kHz. We calibrated the mass axis by recording the time-of-flight of known masses and fitting mass versus time to a quadratic equation. The chemical formulas were inferred from the masses measured.

The pyrolysis experiments were performed by gradually increasing the reactor temperature and recording mass spectra at each temperature. All mass spectra were recorded under identical flow, pressure, and photon-flux conditions, to enable reliable comparison across data sets.

In addition to recording mass spectra as a function of reactor temperature, we recorded mass spectra as a function of photon energy to produce PIE curves at selected reactor temperatures. In these measurements, we recorded mass spectra at 0.05-eV increments for anisole and 0.02-eV increments for 4-vinylnisole over the photon-energy range of 7.7–11.0 eV. This step size provides sufficient energy resolution for species identification with scan lengths short enough to avoid drift of experimental conditions. We generated PIE curves by integrating individual mass peaks at each photon energy over the entire photon-energy range and plotting the integrated ion intensity for each mass peak as a function of photon energy. We averaged 100 000 sweeps for each mass spectrum used in the generation of PIE scans. We corrected for photon-energy-dependent photon flux using the output from a photodiode that measured the beam intensity during the experiments.

These experimental PIE curves were compared with reference data from the literature and established databases to assign chemical identities. This method reduces ambiguity in peak assignments, particularly in cases where multiple isomers have the same nominal mass. PIE scans were produced at selected temperatures, allowing for the identification of both radical and molecular species. The PIE scans were scaled to absolute photoionization cross sections (PICS) to enable estimates of relative species concentrations from measured signals. Previously published PICS values were used when available. When published values were not available, photoionization cross sections were estimated based on analogous species, scaled by the difference in measured ionization energies [100]. For a list of the photoionization cross sections used for this analysis, see Table SI in the Supplemental Material [101].

To establish relative concentrations of reactants and products, signals were corrected for species-dependent absolute photoionization cross section (σ_i) and mass-discrimination factor (α_i), assuming that the signal for species i (S_i) is given by

$$S_{i,T,\lambda} = N_i \alpha_i \sigma_i \rho_T \phi_\lambda, \quad (1)$$

where N_i is the number density, ρ_T is a correction for temperature-dependent density changes, and ϕ_λ is the photon flux at photon energy λ . We expressed α_i

according to

$$\alpha_i = 0.85 \left(\frac{m_i}{30} \right)^{0.55}, \quad (2)$$

which was measured using a configuration similar to that used in the present study [102] and has been scaled to the values of Cool *et al.* [103]. Independently of reactions, the signal was measured to change with the temperature of the reactor (T) according to

$$\rho_T = 1.11 - (4.07 \times 10^{-7})T^{2.04}. \quad (3)$$

We corrected for this temperature dependence in the analysis of the temperature scans to show the product distribution relative to the original reactant concentration at room temperature and to determine whether we were losing species to secondary reactions for which we were not accounting. The relative photon flux was inferred from photodiode measurements. The results were also corrected for natural isotope abundances of carbon and oxygen.

Decomposition pathways were analyzed with the aid of bond dissociation energies calculated using the machine-learning and DFT software ALFABET [104–107]. Mass spectral data were processed using Igor Pro 9 (Wave-metrics, Inc.) [108], which was employed for correcting baselines, integrating signals, correcting for photon flux, plotting temperature-dependent product distributions, identifying onset temperatures for decomposition, visualizing the evolution of intermediates across the temperature range studied, and generating graphics.

III. RESULTS AND DISCUSSION

A. Decomposition of anisole

Figure 4 shows the VUV-PIMS mass spectra of anisole over a range of temperatures at a photon energy of 10.5 eV. A similar figure for a photon energy of 9.5 eV is given in the Supplemental Material [101]. The mass spectra in Fig. 4 show the parent peak for anisole at m/z 108 and pyrolysis-product peaks at m/z 15, 39, 65, 66, 78, 80, 93, 94, and 130. The peak at m/z 58, which appears at room temperature, is likely from residual acetone used to clean the sample holder. Peaks at m/z 20 and 40, apparent at all temperatures at a photon energy of 10.5 eV, are likely attributable to multiphoton ionization of argon for which the peak at m/z 40 is singly charged, and that at m/z 20 is doubly charged. A peak at m/z 40 was observed by Fridrichsen *et al.* [17] in a reactor and at conditions similar to ours. Otherwise, all peaks observed in the mass spectra have been assigned.

Table I provides the assignments for these peaks, which were based on the masses expected during pyrolysis of anisole from previously published results and verified using PICS curves.

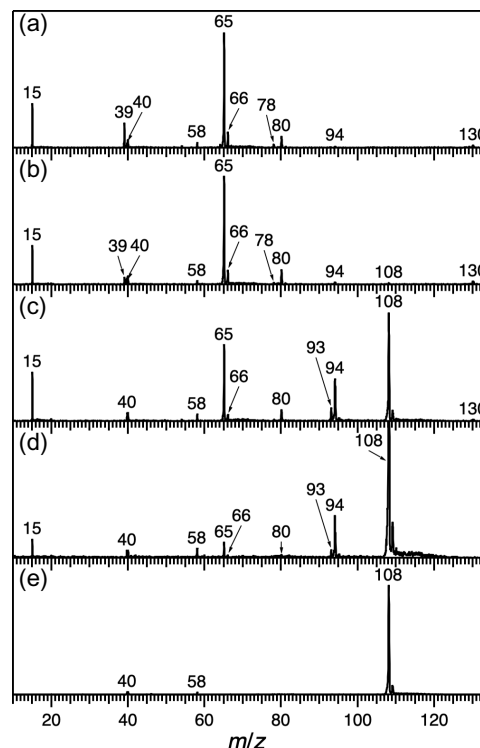


FIG. 4. Photoionization mass spectra of the products of anisole pyrolysis. Mass spectra are shown for pyrolysis temperatures of (a) 1300, (b) 1250, (c) 1150, (d) 1050, and (e) 370 K using a photon energy of 10.5 eV. They are scaled to the highest peak at each temperature. Values of m/z are shown above each peak. These data are available on a Zenodo repository [109].

Figure 5 shows PICS curves for each mass peak listed in Table I. Good agreement is demonstrated with reference curves for each of the assignments given for these peaks in Table I. For m/z 108, the shapes of the PICS curves are the same for temperatures of 370, 800, and 1150 K and are consistent with anisole. At higher temperatures, we may expect the secondary reaction of methyl with phenoxy to form methylcyclohexadienones, which can isomerize to *o*- or *p*-cresol [36,42,50]. Reference curves for methylcyclohexadienones were not available, and our PICS curves appear to be more consistent with anisole than *o*- or *p*-cresol at all temperatures. The magnitude of PICS for anisole shown in Fig. 5 is significantly smaller than that reported by Huang *et al.* [102], which yielded anisole concentrations approximately 4.5 times too low to account for the products observed. We used PICS values for anisole that allowed anisole concentrations to match those of the maximum of the sum of phenoxy, phenol, CPDyl, CPD, MCPD, benzene, propargyl, and $2 \times$ CPDyl dimer.

Figure 6 shows the temperature dependence of individual peaks in these mass spectra, and Fig. 7 summarizes the chemistry responsible for the products observed. In Fig. 6, the parent anisole peak (m/z 108) decreases as the temperature increases and completely disappears by 1250 K.

TABLE I. Peak assignments for anisole pyrolysis.

m/z	Peak assignment	Chemical structure
15	Methyl radical	$\bullet\text{CH}_3$
39	Propargyl radical	$\text{C}\equiv\text{C}-\text{CH}_2\bullet$
65	Cyclopentadienyl radical	
66	Cyclopentadiene	
78	Benzene	
80	Methylcyclopentadiene	
93	Phenoxy radical	
94	Phenol	
108	Anisole	
130	Cyclopentadienyl dimer (Fulvalene)	

The phenoxy-radical peak (m/z 93) and the methyl peak (m/z 15) start to appear at approximately 1050 K as the anisole peak decreases. These first products observed result from the breaking of the O—CH₃ bond, the first step in the pyrolytic decomposition of anisole.

As shown in Fig. 7, the cleavage of the O—CH₃ bond produces the phenoxy radical (m/z 93), an important intermediate in many combustion systems [17,18,21,27,32,36,40,42,44,45]. The bond dissociation energy (BDE) of the O—CH₃ bond has been calculated to be 64.9 kcal/mol by Breuer *et al.* [6], 64.7 kcal/mol by Li *et al.* [47], 63.7 kcal/mol by Zhang *et al.* [35], 63.2 kcal/mol by Nowakowska *et al.* [34], and 63.90 ± 0.23 kcal/mol for 0 K from the Active Thermochemical Tables Version 1.220 (ATcT) [121–123]. The BDE has been measured to be 64 kcal/mol by Friderichsen *et al.* [17], 61.7 ± 0.3 kcal/mol by Scheer *et al.* [40], 65.30 kcal/mol by Pratt *et al.* [124], 65.4 ± 0.30 kcal/mol by Mulder *et al.* [125], and 63.5 kcal/mol by Suryan *et al.* [55].

Previous work has shown that the phenoxy radical readily combines with hydrogen to form phenol [18,21,36,42,43], which appears at the same temperature as phenoxy (1050 K). Phenoxy and phenol reach a maximum at 1150 K and disappear at higher temperatures.

Phenoxy additionally decomposes to form the RSR cyclopentadienyl radical (CPDyl) (m/z 65) and CO [17,18,21,28,32,36,40,42,43,126]. In Fig. 6, CPDyl appears at the same temperature as phenoxy, 1050 K, signaling the immediate decomposition of phenoxy into CPDyl and CO. The ionization energy (IE) of CO (14.014 ± 0.0003 eV [127]) is too high for detection at the photon energies used in our experiments.

CPDyl can dimerize, which generates a peak at m/z 130 (C₁₀H₁₀) at 1100 K [17,40,128–132]. The structure shown in Fig. 7 (fulvalene) is the product predicted by the work of Long *et al.* [133] to be formed in low-pressure regimes (<1 atm). Li *et al.* [110] similarly observed this dimer formation during anisole pyrolysis but did not record a PIE curve at low enough photon energies to provide the estimated adiabatic ionization energy. Our PICS curve shown in Fig. 5(a) yields an ionization energy of 7.90 ± 0.05 eV. Previous work has shown that fulvalene can isomerize and lose hydrogen to form naphthalene (m/z 128) at significantly longer residence times [17,129], higher concentrations [40,48], or higher pressures than those used in our experiments [133]. Under our conditions, naphthalene formation was negligible.

Scheer *et al.* [40] showed that, at high temperature, CPDyl decomposes into acetylene (m/z 26) and propargyl radical (m/z 39), the latter of which is also an RSR. Our results demonstrate the formation of propargyl at 1200 K. We were unable to detect acetylene ($\text{IE} = 11.4 \pm 0.05$ eV [134]) with the photon energies used in these experiments.

CPDyl also reacts with the methyl radical to form methylcyclopentadiene (MCPD) (m/z 80) [18,21,36,40,42,131], which appears at 1050 K in our mass spectra, signaling a radical recombination reaction between methyl and CPDyl. Carpenter *et al.* [49] suggested that MCPD may alternatively be produced via recombination of methyl with phenoxy to form methylcyclohexadienones and cresols, which may first lose an H atom to form methylphenoxy and then CO to form MCPD. We, however, see no evidence of methylphenoxy formation. MCPD undergoes multiple hydrogen abstractions and a ring enlargement to form benzene (m/z 78) [36,40,43,135], which appears in Fig. 6 at approximately 1200 K. Although the concentration and signal for benzene are small compared to the other species, the signal-to-noise ratio for benzene was >10 at temperatures greater than 1100 K, and we were able to verify its identity via comparison with PICS reference curves. Propargyl radicals can recombine to form benzene (m/z 78) [49,136,137], thereby providing another route to the formation of benzene [40]. Scheer *et al.* [40] concluded that benzene is predominantly formed

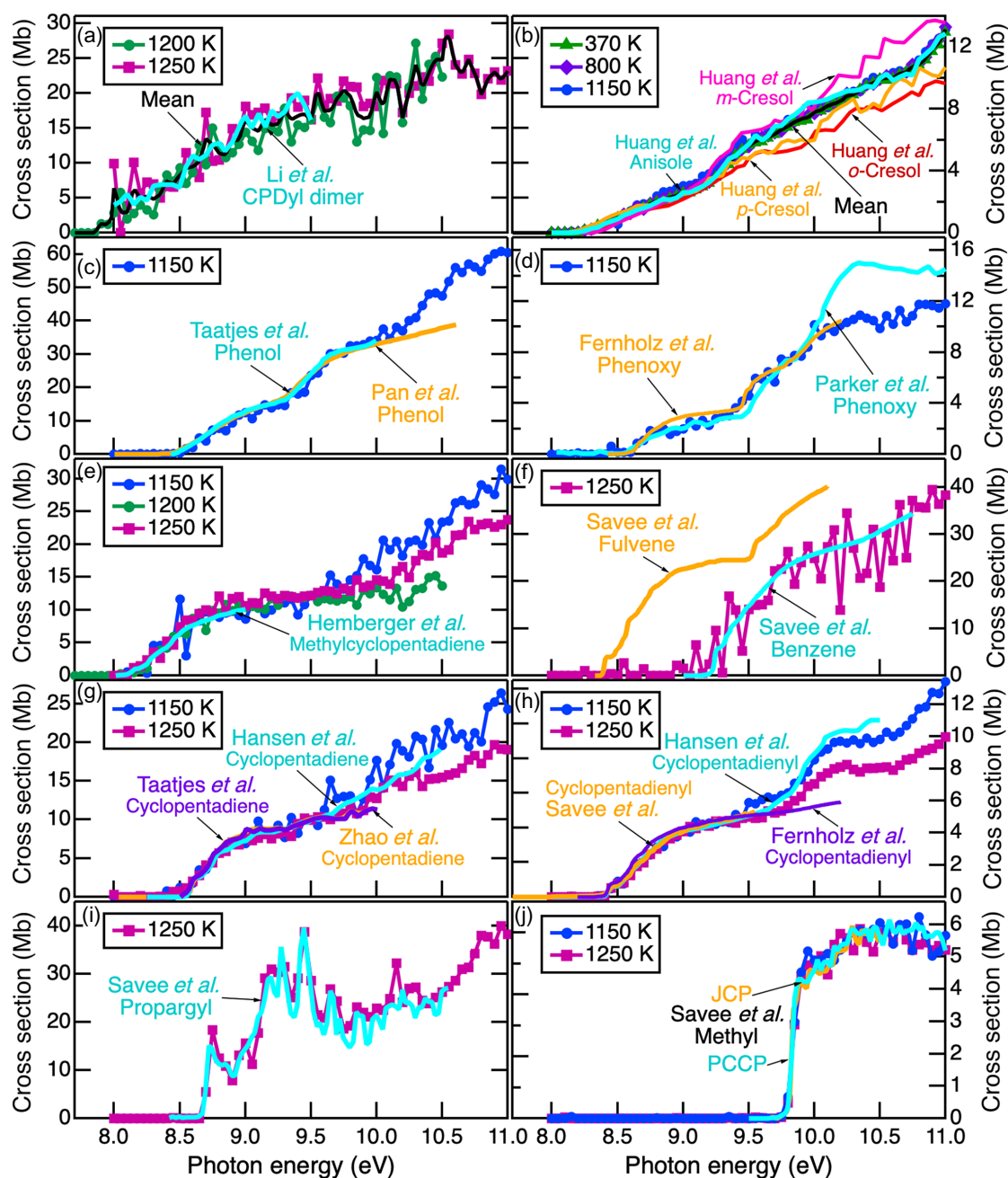


FIG. 5. Photoionization cross sections for anisole and products of its pyrolysis. PICS curves are shown for peaks from anisole pyrolysis at m/z (a) 130, (b) 108, (c) 94, (d) 93, (e) 80, (f) 78, (g) 66, (h) 65, (i) 39, and (j) 15. Measured curves from this study are shown as symbols. Averages of measured curves are shown as solid black lines. Pyrolysis temperatures are provided in the legends. Reference curves are shown as solid colored lines for (a) cyclopentadienyl dimer (fulvalene) from Li *et al.* [110] scaled to PICS from cyclopentadiene, assuming $IE(CPD) - IE(fulvalene)$ is 0.74 eV, (b) anisole, *o*-cresol, *m*-cresol, and *p*-cresol from Huang *et al.* [102] scaled to be consistent with our results (see text), (c) phenol, derived from a threshold photoelectron spectrum (TPES) from Taatjes *et al.* [111] and Pan *et al.* [112] scaled to Taatjes *et al.* [111], (d) phenoxy from Parker *et al.* [113] and from the TPES from Fernholz *et al.* [114] scaled to the PICS from Xu and Pratt [115], (e) methylcyclopentadiene, derived from the TPES from Hemberger *et al.* [116] scaled to 1,3-cyclopentadiene using a difference in ionization energies, $IE(CPD) - IE(MCPD)$, of 0.54 eV, (f) fulvene and benzene, derived from TPE spectra from Savee *et al.* [100], (g) cyclopentadiene from Taatjes *et al.* [111], Zhao *et al.* [86], and Hansen *et al.* [117] scaled to Taatjes *et al.* [111], (h) cyclopentadienyl from Savee *et al.* [85], Hansen *et al.* [117], and the TPES of Fernholz *et al.* [114] scaled to PICS from Herbinet *et al.* [118], (i) propargyl from Savee *et al.* [119], and (j) methyl from Savee *et al.* [119,120]. The PICS data and reference curves used for this figure are provided in the Supplemental Material [101]. The raw mass-spectrometer data are available on a Zenodo repository [109].

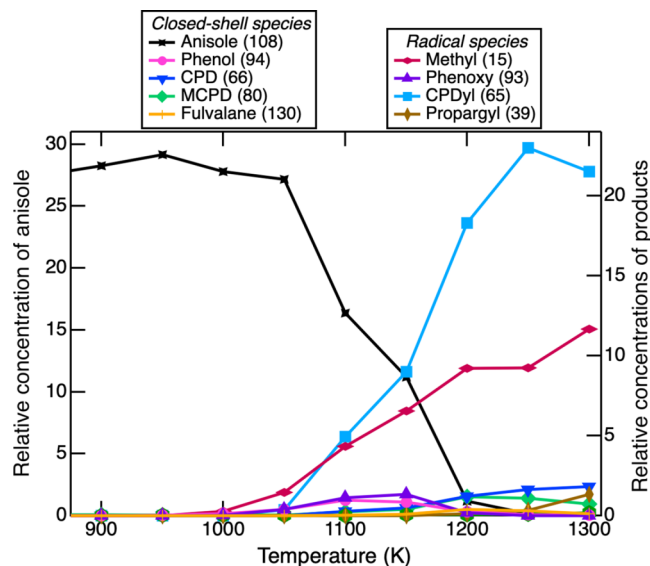


FIG. 6. The temperature dependence of anisole and selected products of its pyrolysis. Integrated peaks at m/z of 15, 39, 65, 66, 80, 93, 94, 130, and 108 are plotted as a function of the pyrolysis temperature. The associated mass spectra were recorded using a photon energy of 9.5 eV; for methyl, the mass spectra were recorded with a photon energy of 10.5 eV. The product signals are plotted relative to the scale on the right axis. The anisole signal is shown relative to the left axis. The processed temperature-scan data used for this figure are provided in the Supplemental Material [101]. The raw mass-spectrometer data are available on a Zenodo repository [109].

via MCPD decomposition during anisole pyrolysis, but a reanalysis of their data suggests that the two routes to benzene formation were competitive under their experimental conditions [49]. Li *et al.* [46] concluded that benzene formation during 4-MA pyrolysis proceeds via the MCPD decomposition pathway rather than via propargyl dimerization.

B. Decomposition of 4-vinylnisole

To date, there have been no reported detailed mechanistic studies of the pyrolysis of 4-vinylnisole (4-VA). Figure 8 shows mass spectra of the pyrolysis products of 4-VA over a range of pyrolysis temperatures and a photon energy of 10.5 eV. A mass spectrum recorded at a photon energy of 9.5 eV is presented in the Supplemental Material [101]. For 4-VA, the parent peak is at m/z 134, and the major pyrolysis-product peaks are at m/z 15, 39, 52, 65, 89, 90, 91, 92, 106, 118, 119, and 120. At low temperatures, there is a minor contamination peak at m/z 108 from running anisole in our system just before these experiments, but it disappeared with increasing temperature (and time during our experimental run) and did not appear to contaminate the products. There is also a peak at m/z 40, which is apparent at all temperatures at 10.5 eV and is

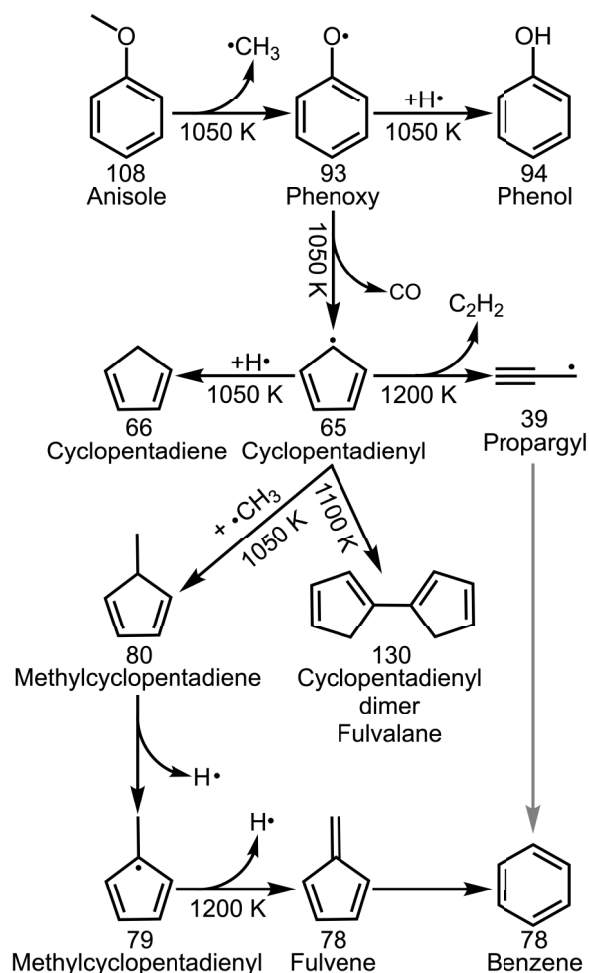


FIG. 7. Pathways to decomposition products during anisole pyrolysis. Structures are shown for decomposition products. The numbers under the structures represent molecular masses in daltons (i.e., m/z peak locations). The name of each species is listed under its molecular mass. Temperatures at which we first observed reaction products are also noted.

likely attributable to multiphoton ionization of argon. Otherwise, all peaks observed in the mass spectra have been assigned.

Table II provides the identifications for these peaks, which were based on species hypothesized to be formed during 4-VA pyrolysis and verified, where possible, using PICS comparisons with reference curves.

Figure 9 shows PICS curves for each mass peak listed in Table II. Good agreement is demonstrated with reference PICS curves for 7 of the 13 assignments given in Table II (m/z 15, 39, 52, 65, 89, 90, and 91). Reference curves were not available for 4-vinylnisole (m/z 134), 4-vinylphenol (m/z 120), 4-vinylphenoxy (m/z 119), dimethylfulvene (m/z 106), and vinylcyclopentadiene (m/z 92).

Our ionization energy for m/z 91 is 7.82 ± 0.02 eV, which is consistent with ionization energies reported by

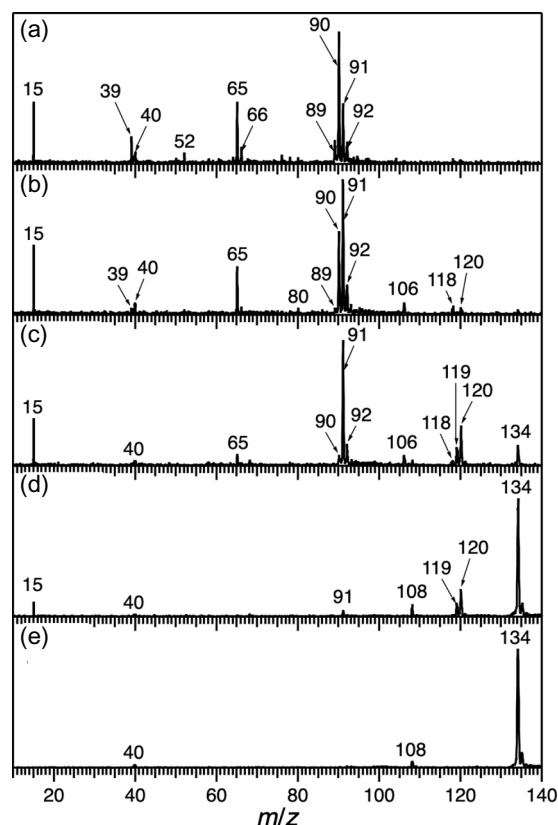


FIG. 8. Photoionization mass spectra of the products of 4-vinylanisole pyrolysis. Mass spectra are shown for pyrolysis temperatures of (a) 1300, (b) 1200, (c) 1100, (d) 1000, and (e) 400 K using a photon energy of 10.5 eV. They are scaled to the highest peak at each temperature. Values of m/z are shown above each peak. These data are available on a Zenodo repository [109,143].

Jin *et al.* [83] and McClish *et al.* [84] for vinylcyclopentadienyl radical.

We identified m/z 92 in our experiments as vinylcyclopentadiene, with an ionization energy of 7.95 ± 0.05 eV. Toluene and fulvenone have a mass of 92 Da but higher ionization energies than that of the isomer measured in our experiments at this mass. The adiabatic ionization energy of fulvenone is 8.35 ± 0.01 eV [144] and that of toluene is between 8.82 [145,146] and 8.86 ± 0.05 eV [147].

The ionization energy of 7.95 ± 0.10 eV for the peak at 106 Da most closely agrees with the ionization energy for 6,6-dimethylfulvene measured and calculated to be 8.05 eV [138,148]. Other isomers include ethylbenzene, which has an ionization energy of 8.77 eV, *o*-, *m*-, and *p*-xylene, which have ionization energies in the range of 8.46–8.55 eV, and benzaldehyde, which has an ionization energy of 9.50 eV [146]. The IE for 1,3,5-cyclooctatriene is 7.9 eV [86], which also gives agreement with our measured IE for m/z 106, but formation of this species is less probable than 6,6-dimethylfulvene production.

TABLE II. Peak assignments for 4-vinylanisole pyrolysis.

m/z	Peak assignment	Chemical structure
15	Methyl radical	$\bullet\text{CH}_3$
39	Propargyl radical	$\text{C}\equiv\text{C}-\text{CH}_2\bullet$
52	Vinylacetylene	$\text{C}\equiv\text{C}-\text{CH}=\text{CH}_2$
65	Cyclopentadienyl radical	
89	Fulvenallenyl radical	
90	Fulvenallene	
91	Vinylcyclopentadienyl radical	
92	Vinylcyclopentadiene	
106	6,6-Dimethylfulvene	
119	4-Vinylphenoxy radical	
120	4-Vinylphenol	
134	4-Vinylanisole	

We identified peaks at 119 Da as 4-vinylphenoxy with an IE of 8.02 ± 0.02 eV, 120 Da as 4-vinylphenol with an IE of 8.08 ± 0.02 eV, and 134 Da as 4-vinylanisole with

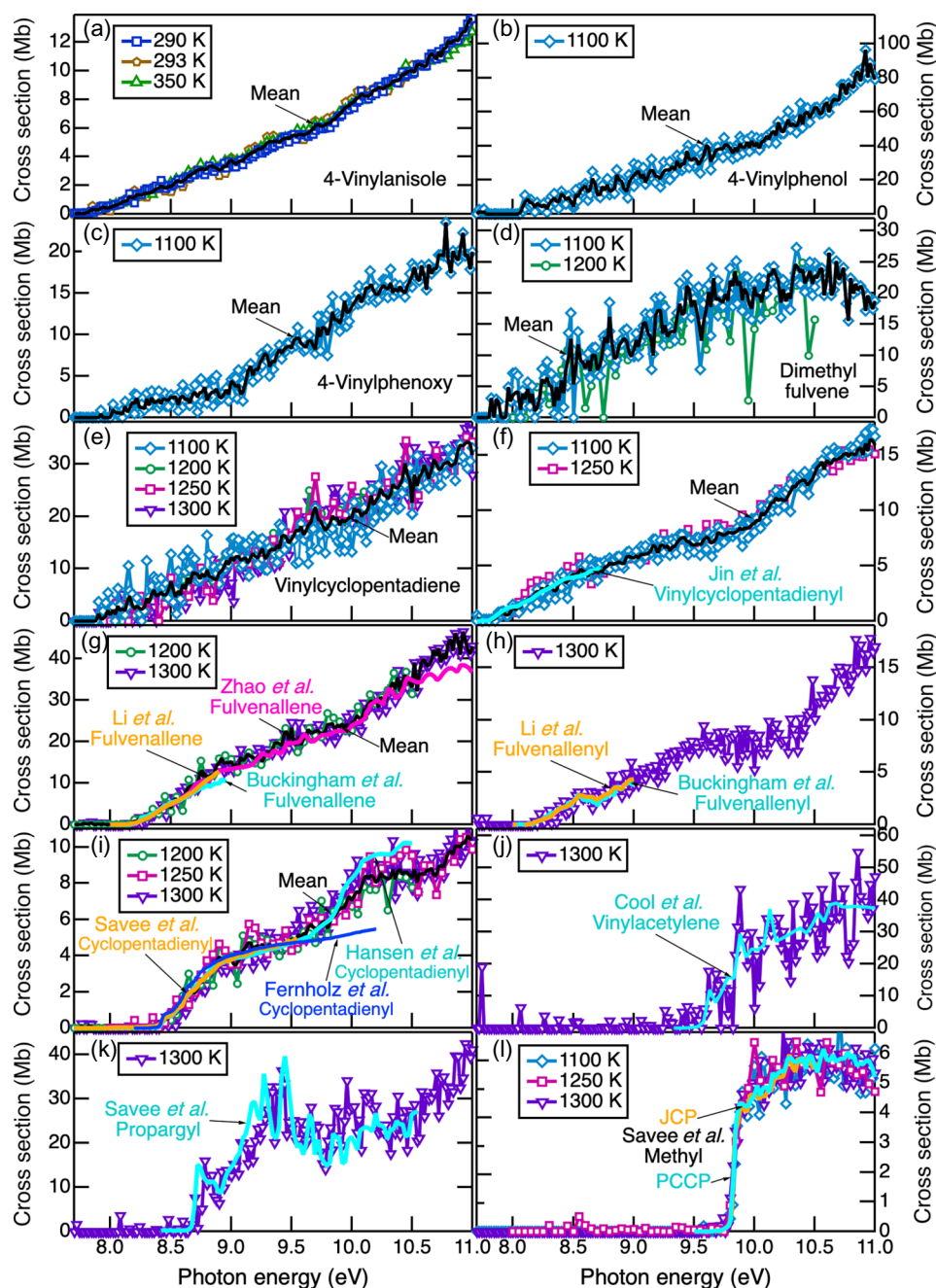


FIG. 9. Photoionization cross sections for 4-vinylanisole and products of its pyrolysis. PICS curves are shown for peaks at m/z of (a) 134, (b) 120, (c) 119, (d) 106, (e) 92, (f) 91, (g) 90, (h) 89, (i) 65, (j) 52, (k) 39, and (l) 15. Measured curves from this study are shown as symbols. Averages of measured curves are shown as solid black lines. Pyrolysis temperatures are provided in the legends. PIEs for (a) vinylanisole were scaled to be consistent with our data (see text), (b) vinylphenol were scaled to phenol, assuming that $\text{IE}(\text{phenol}) - \text{IE}(4\text{-vinylphenol})$ is 0.44 eV, for (c) vinylphenoxy were scaled to phenoxy, assuming that $\text{IE}(\text{phenoxy}) - \text{IE}(4\text{-vinylphenoxy})$ is 0.54 eV, for (d) 6,6-dimethylfulvene were scaled to values estimated from Palmer *et al.* [138], and for (e) vinylcyclopentadiene were scaled to cyclopentadiene, assuming that $\text{IE}(\text{CPD}) - \text{IE}(\text{VCPD})$ is 0.64 eV. Reference cross sections are shown as solid colored lines for (f) vinylcyclopentadienyl from Jin *et al.* [83] scaled to cyclopentadienyl assuming that the difference $\text{IE}(\text{CPDyl}) - \text{IE}(\text{VCPDyl})$ is 0.62 eV, (g) fulvenallene from Buckingham *et al.* [139], Zhao *et al.* [86], and Li *et al.* [140] scaled to Li *et al.* [140], (h) fulvenallenyl from Buckingham *et al.* [139] and Li *et al.* [140] scaled to Jin *et al.* [141], (i) cyclopentadienyl from Savee *et al.* [85], Hansen *et al.* [117], and the TPES of Fernholz *et al.* [114] scaled to PICS from Herbinet *et al.* [118], (j) vinylacetylene from Cool *et al.* [142], (k) propargyl from Savee *et al.* [119], and (l) methyl from Savee *et al.* [119,120]. The PICS data and reference curves used for this figure are provided in the Supplemental Material [101]. The raw mass-spectrometer data are available on a Zenodo repository [109,143].

an IE of 7.82 ± 0.02 eV. PICS values for 4-vinylanisole were determined to allow the initial 4-VA concentrations to match those of the maximum of the sum of 4-vinylphenoxy, 4-vinylphenol, VCPDyl, VCPD, CPDyl, fulvenallene, fulvenallenyl, propargyl, vinylacetylene, and dimethylfulvene.

Figure 10 shows the temperature dependence of the products observed in our experiments, and Fig. 11 summarizes the pathways to 4-VA decomposition proposed to explain these observations. Under our pyrolysis conditions, for which the residence time in the heated region of the reactor was in the range of 30–80 μ s, bond cleavage occurs in 4-VA at approximately 900 K. With our 50-K temperature resolution, m/z 15 and m/z 119 first appear at 900 K as 4-VA decomposes into vinylphenoxy radical (m/z 119) and methyl radical (m/z 15). With a pyrolysis residence time of nearly 10 s (more than 10^5 times longer than ours), Hendrick *et al.* [82] observed m/z 119 during 4-vinylanisole pyrolysis at 723 K.

As shown in Fig. 11, the first step in the decomposition of 4-VA is the cleavage of the O—CH₃ bond. Chen *et al.* [60] predicted that 4-vinylanisole pyrolysis will form the 4-vinylphenoxy radical with a BDE for the O—CH₃

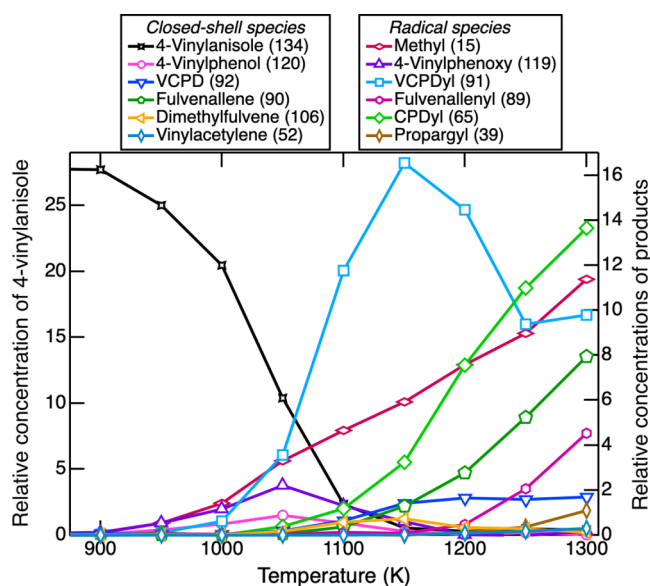


FIG. 10. The temperature dependence of the signal from 4-VA and selected products of its pyrolysis. Integrated peaks at m/z of 15, 39, 65, 89, 90, 91, 92, 106, 119, 120, and 134 are plotted as a function of the pyrolysis temperature. The associated mass spectra were recorded using a photon energy of 9.5 eV; for methyl and vinylacetylene, the mass spectra were recorded with a photon energy of 10.5 eV. The product signals are plotted relative to the scale on the right axis. The 4-vinylanisole signal is shown relative to the left axis. The processed temperature-scan data used for this figure are provided in the Supplemental Material [101]. The raw mass-spectrometer data are available on a Zenodo repository [109,143].

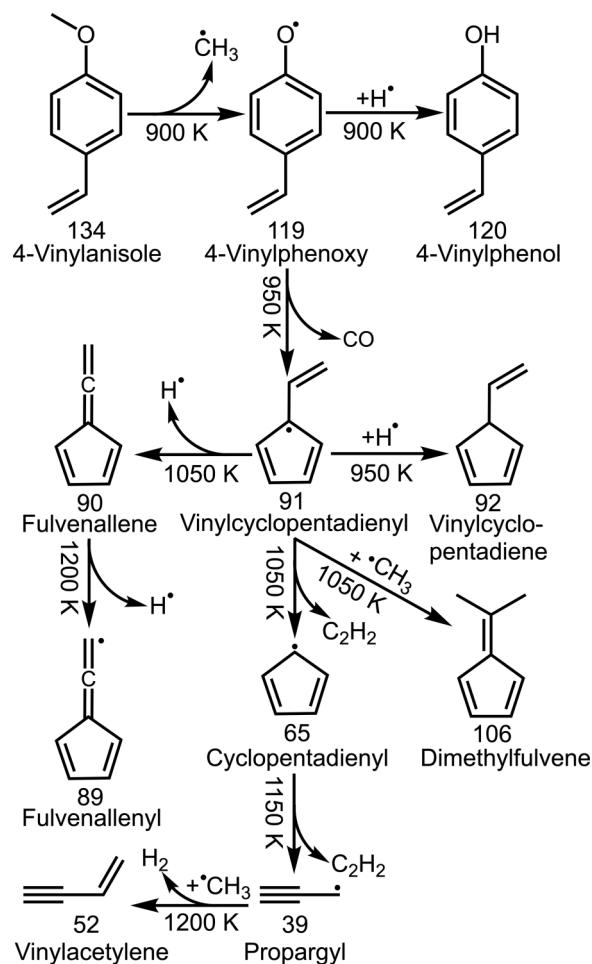


FIG. 11. Pathways to decomposition products during 4-vinylanisole pyrolysis. Structures are shown for decomposition products. The numbers under the structures represent molecular masses in daltons (i.e., m/z peak locations). The name of each species is listed under its molecular mass. Temperatures at which we first observed reaction products are also noted.

bond of 52.37 kcal/mol. This value is significantly smaller than the values of 63.2–65.4 kcal/mol calculated for the O—CH₃ bond in anisole. The DFT calculations from ALFABET [104–107] provide values for the bond dissociation energy of the O—CH₃ bond of 69.3 kcal/mol for anisole and 65.9 kcal/mol for 4-VA. These results suggest that the bond energy is lowered by the addition of the vinyl group to the aromatic ring and are consistent with the theoretical work of Suryan *et al.* [55] for ortho-substituted vinylanisole.

At temperatures of 900 K and above, the vinylphenoxy radical reacts with hydrogen and forms vinylphenol (m/z 120), as predicted by Chen *et al.* [60]. Yin *et al.* [62] similarly observed 4-vinylphenol during the pyrolysis of a model lignin polymer of *p*-hydroxyphenyl. Pyrolysis of herbaceous lignin typically produces 4-vinylphenol [63,64]. At 950 K, vinylcyclopentadienyl radical (VCPDyl)

(m/z 91) appears. VCPDyl is an important C_7H_7 radical intermediate frequently observed during the initial formation of soot [149–152]. During 4-VA pyrolysis, we infer by analogy with anisole that VCPDyl is formed when the vinylphenoxy radical undergoes decomposition by losing CO. VCPDyl readily reacts with hydrogen to form a species at m/z 92, which we infer by analogy with anisole-pyrolysis chemistry to be vinylcyclopentadiene (VCPD) (also known as 5-ethenylcyclopenta-1,3-diene). Simultaneously with the appearance of VCPDyl (at 950 K), VCPD is formed.

Previous work has suggested that VCPDyl loses acetylene (m/z 26) to form CPDyl (m/z 65) [151,153]. CPDyl starts to form at approximately 1050 K, but we did not observe acetylene because its ionization energy is higher than the photon energies used here. Hendrick *et al.* [82] also observed m/z 65 during 4-vinylnisole pyrolysis. At 1050 K, VCPDyl also loses a hydrogen atom to form fulvenallene (m/z 90) and reacts with methyl to form the adduct at m/z 106, which we hypothesize is 6,6-dimethylfulvene. This adduct formation is analogous to the formation of MCPD by the reaction of CPDyl with methyl during anisole pyrolysis. At 1200 K, fulvenallene loses a hydrogen atom to form the RSR fulvenallenyl (m/z 89).

As discussed above for anisole, CPDyl decomposes into acetylene (m/z 26) and propargyl radicals (m/z 39); we observed propargyl at a temperature of 1150 K. We also observed vinylacetylene (m/z 52) at 1200 K, and we hypothesize that it is formed by the reaction of propargyl with methyl radicals.

For 4-VA, we did not see evidence of benzene formation. Sood *et al.* [24] predicted that benzofuran (m/z 118) may be produced in the decomposition of 4-vinylphenoxy. We see the appearance of m/z 118 at 1050 K, and its PIE curve is consistent with that of benzofuran from Ma *et al.* [154], as shown in Fig. S5 in the Supplemental Material [101]. Alternatively, 4-ethynylphenol (m/z 118) may be produced from 4-vinylphenoxy via the loss of a hydrogen atom and hydrogen migration or from 4-vinylphenol via the loss of two hydrogen atoms from the vinyl group. We do not have a PIE reference curve for 4-ethynylphenol, and our signal at m/z 118 is too noisy for a definitive identification. The identity of m/z 118 is thus speculative.

C. Comparison of anisole and 4-VA pyrolysis

The initial step in the decomposition of both anisole and 4-vinylnisole is the cleavage of the O—CH₃ bond. The energy required to break this bond is estimated to be lower for 4-VA than for anisole by 3.4 kcal/mol based on ALFA-BET DFT calculations [104–107]. This difference could be as large as 13 kcal/mol, based on calculations by Chen *et al.* [60] for 4-VA compared to measured [55,124,125]

and calculated [6,34,35,47,121–123] values for anisole. The BDE for 4-VA is lower than that for anisole because the vinyl substitution (1) is electron donating and (2) extends the resonance stabilization of the phenoxy radical produced when the bond is broken. The consequence of this lower bond energy is that this bond breaks at a lower temperature range (900–950 K) for 4-VA than for anisole (1000–1050 K). Table III shows the important analogous decomposition products of anisole and 4-VA.

The temperature-dependence curves for the pyrolysis of both species, Figs. 6 and 10, show that CPDyl from anisole forms at approximately 1050 K, the same temperature at which it forms from VCPDyl. For anisole, this temperature is the same as that at which phenoxy and phenol are formed; thus, for anisole, the CPDyl-production pathway competes with phenol production as soon as phenoxy is produced. For 4-VA, on the other hand, vinylphenoxy and vinylphenol are produced at slightly lower temperatures than VCPDyl, which allows vinylphenoxy and vinylphenol to form at temperatures below that at which the VCPDyl pathway depletes vinylphenoxy during 4-VA pyrolysis. This mechanism may explain why 4-vinylphenol is readily observed during lignin pyrolysis. Vinylphenoxy and vinylphenol reach a maximum at 1050 K, which is in the range of temperatures typically used for lignin pyrolysis and observed during biomass pyrolysis in wildfires [64,155]. VCPDyl production overtakes vinylphenol production at a temperature between 1000 and 1050 K.

The peak of CPDyl from anisole pyrolysis is at approximately 1250 K, and for VCPDyl, the peak is at approximately 1150 K. Although VCPDyl can form VCPD by taking on a hydrogen at temperatures of 950 K, this loss pathway is slower than decomposition of VCPDyl into fulvenallene by losing a hydrogen at temperatures higher than 1150 K or forming CPDyl by losing an acetylene at temperatures 1100 K and higher. Reaction of VCPDyl with methyl to form an adduct at m/z 106 also competes with VCPD formation at temperatures above 1050 K.

During anisole pyrolysis, CPDyl does not have an available fulvenallene-type pathway (a simple hydrogen-loss mechanism). Instead, it forms methylcyclopentadiene (MCPD) by reacting with methyl radical and then continues to formation of benzene. It also forms CPD and

TABLE III. Analogous structures produced by anisole and 4-vinylnisole pyrolysis.

Anisole pyrolysis	4-VA pyrolysis
Anisole	4-Vinylnisole
Phenoxy radical	4-Vinylphenoxy radical
Phenol	4-Vinylphenol
CPDyl radical	VCPDyl radical
MCPD	Dimethylfulvene

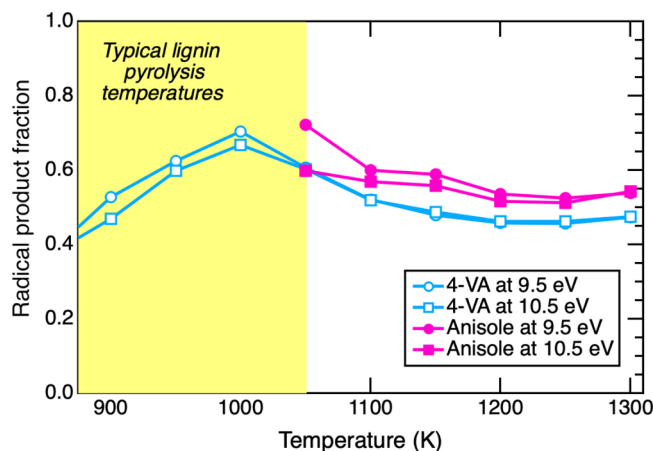


FIG. 12. The fraction of products that are radicals by number density. The sums of radical species measured for anisole and 4-vinylanisole (4-VA) pyrolysis are divided by the total measured species and plotted as a function of temperature (see text for details). The shaded region indicates the temperature range over which lignin decomposition occurs [155].

CPDyl dimer. At higher temperatures, it decomposes into propargyl and acetylene.

Much less CPDyl is formed during 4-VA pyrolysis than during anisole pyrolysis and, as a result, decomposition to propargyl and acetylene dominates over radical recombination of CPDyl with hydrogen to form CPD, with methyl to form MCPD, or with itself to form CPDyl dimer. Benzene formation thus occurs during anisole pyrolysis but not during 4-VA pyrolysis; this lack of benzene production during 4-VA pyrolysis is consistent with MCPD being the predominant intermediate in benzene formation during anisole pyrolysis.

In general, however, both anisole and 4-VA form radicals as a large fraction of their product number densities. All of the radicals we measure are RSRs, except for methyl. Hydrogen atoms will play a very important role in propagating radical formation, particularly at higher temperatures for which unimolecular hydrogen ejection becomes viable [156]. Hydrogen ejection likely occurs at approximately 1050 K in 4-VA pyrolysis, leading to the formation of fulvenallene from VCPDyl. It may occur at temperatures closer to 1200 K for anisole, leading to the eventual formation of benzene from MCPD. Reactions involving hydrogen at lower temperatures likely occur via abstraction, such as the abstraction of a hydrogen by phenoxy to form phenol.

Figure 12 shows a comparison of the estimated fraction of products that appear in our experiment to be radicals. We have attempted to account for hydrogen-atom, CO, and acetylene production by assuming that every species for which H, CO, or C_2H_2 is a byproduct in its production can be used as a proxy for that byproduct.

For 4-VA, CO is estimated as the sum of VCPDyl, VCPD, fulvenallene, fulvenallenyl, dimethylfulvene, CPDyl, propargyl, and vinylacetylene. One CO molecule is produced during the formation of one molecule of each of these species. Acetylene is the sum of CPDyl, $2 \times$ propargyl, and $2 \times$ vinylacetylene. Hydrogen atom is assumed to be the sum of fulvenallene and $2 \times$ fulvenallenyl.

For anisole, CO is estimated as the sum of CPDyl, CPD, propargyl, MCPD, benzene, and fulvalene. Acetylene is accounted for by propargyl, and hydrogen atom is represented by $2 \times$ benzene.

As demonstrated in Fig. 12, radicals account for more than 40% of the products during anisole and 4-VA pyrolysis at all temperatures for which products are formed. The reason the radical fraction is less than 100% initially is because phenoxy and vinylphenoxy very rapidly form closed-shell secondary products, vinylphenol (at 900 K) in the case of 4-VA pyrolysis and phenol (at 1050 K) in the case of anisole pyrolysis. If we were to weight these results by mass or carbon number, the fraction apportioned to radicals would be much higher.

D. Connection between vinyl substitutions and char-tar and particle formation in lignin pyrolysis

Previous work has suggested that vinyl-substituted aromatic products in lignin pyrolysis are associated with enhanced char and tar formation, compared to alkyl (including methyl) and methoxy substituents [8,16]. With respect to substituted anisoles, methyl and vinyl substitutions weaken the $O-CH_3$ bond, but the relative influence of these substituents on the BDE is not clear. Whether or not they weaken the bond to the same extent and thus initiate pyrolytic decomposition similarly, the increased char formation with vinyl substitution (over methyl substitution) is likely attributable to the pyrolysis products, rather than to the initial bond-cleavage propensity.

Figure 13 summarizes pathways for the decomposition of 4-MA [46,47]. The main products observed during 4-MA decomposition at temperatures above 1200 K are the methyl radical and the closed-shell species benzene and 4-methylene-2,5-cyclohexadiene-1-one [46,47].

The main products of 4-VA at these temperatures, on the other hand, are hydrogen atoms and methyl radicals, the RSR species CPDyl, VCPDyl, and fulvenallenyl, fulvenallene, VCPD, fulvalene, vinylacetylene, CO, and acetylene. CPDyl, VCPDyl, fulvenallenyl, and methyl can drive radical-chain reactions to initiate the transition from gas-phase species to condensed-phase char or tar products, such as by the clustering of hydrocarbons by radical-chain reactions (CHRCR) mechanism [149]. Fulvenallene is unsaturated and can also participate in the CHRCR mechanism to generate char and tar. This hypothesis is consistent with previous work suggesting that vinyl

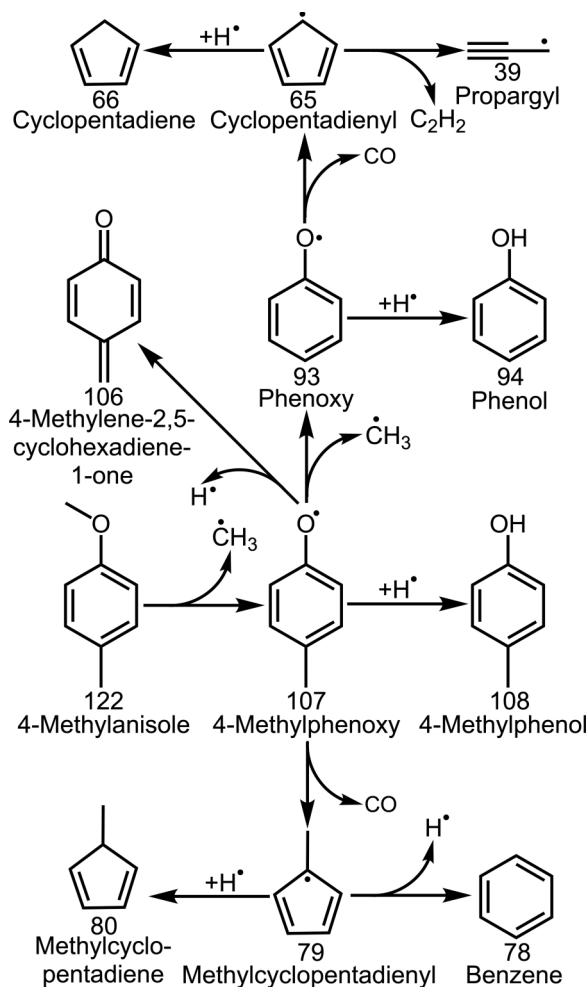


FIG. 13. Pathways to decomposition products during 4-methylanisole pyrolysis. Structures are shown for decomposition products. The numbers under the structures represent molecular masses in daltons (i.e., m/z peak locations). The name of each species is listed under its molecular mass. The pathways shown for 4-MA pyrolysis were proposed by Li *et al.* [46,47].

side chains in lignin pyrolysis products are highly reactive toward repolymerization [16]. The products of 4-MA are less reactive and less likely to polymerize through a CHRCR-like mechanism.

Char can also be formed during anisole pyrolysis [157]. The main pyrolysis product of anisole above 1200 K is CPDyl, which can readily participate in CHRCR-type clustering reactions to form char or tar. At lower temperatures, however, the vinyl-substituted species is more likely to form such byproducts because they start to decompose at a lower temperature than the unsubstituted species. Decomposition of lignin largely occurs in the range of 550–1050 K [155]. This temperature range is thus relevant for wildfire emissions associated with biomass pyrolysis and biofuel production [64,155] (see Fig. 12). In this temperature range, under our experimental conditions, 4-VA decomposes and produces radicals, but anisole produces

radicals only at the very high edge of this temperature range, as shown in Fig. 12. Under production applications or wildfire conditions, with longer residence times (on the order of seconds), anisole may decompose, but 4-VA would generate significantly more radicals than would anisole. Thus, 4-VA would be more likely than anisole to form char and tar during biofuel-production applications and soot precursors during wildfire pyrolysis.

A detailed study by Akherati *et al.* [4] showed that biomass burning produces significant oxygenated aromatics, which act as effective precursors for secondary organic aerosols (SOAs). In a series of biomass-burning experiments that produced 20% oxygenated aromatics in the gas phase, the SOAs produced were composed of 60% oxygenated aromatics, all of which were phenol or substituted phenols. Our results demonstrate that 4-VA is more likely to produce a phenol product than either anisole or 4-MA. In addition, at slightly higher temperatures, the RSRs formed by anisole and 4-VA can readily participate in particle formation via the CHRCR mechanism.

IV. CONCLUSIONS

We have studied and compared the pyrolysis of anisole and 4-vinylanisole. Our results for the pyrolysis of anisole are consistent with many previous similar studies [17,18,21,28,32,36,40,42,43,46,47,126]. This work expands on previous work on the pyrolysis of substituted anisole, which has largely been focused on methyl and electron-donating- and electron-withdrawing-group substitutions on the benzene ring. The initial route of decomposition for both anisole and 4-vinylanisole is the cleavage of the O—CH₃ bond. The temperature at which this bond cleavage occurs is lower for 4-VA than for anisole. The primary products of anisole decomposition are hydrogen-atom, methyl, propargyl, cyclopentadienyl, and phenoxy radicals, cyclopentadiene, phenol, methylcyclopentadiene, cyclopentadienyl dimer (fulvalene, C₁₀H₁₀), CO, and acetylene. A small amount of benzene is also produced. For 4-VA, the products differ from those of anisole in part because the vinyl substitution on the benzene ring of 4-VA weakens the O—CH₃ bond, which initiates decomposition at lower temperatures than for anisole.

Cyclopentadienyl (CPDyl) is formed at the same temperature during anisole and 4-VA pyrolysis. During 4-VA pyrolysis, however, vinylcyclopentadienyl (VCPDyl) is formed at a lower temperature than CPDyl and is readily converted to fulvenallene, vinylcyclopentadiene (VCPD), and an adduct with methyl, which limits the production of CPDyl from 4-VA pyrolysis.

Anisole pyrolysis, on the other hand, forms methylcyclopentadiene (MCPD) through the radical-recombination reaction of methyl with CPDyl. MCPD loses a hydrogen atom to form methylcyclopentadienyl (MCPDyl), which loses another hydrogen atom to form benzene. This

pathway and its product, benzene, are not observed for 4-VA because CPDyl decomposes too rapidly to form the MCPD intermediate to benzene formation. The main products of 4-VA pyrolysis are hydrogen-atom, methyl, propargyl, vinylphenoxy, VCPDyl, CPDyl, and fulvenallenyl radicals, vinylphenol, fulvenallene, VCPD, an adduct of VCPDyl with methyl (possibly dimethylfulvene), vinylacetylene, and a product with m/z 118 (e.g., benzofuran or 4-ethynylphenol).

Our results suggest that more facile char formation with vinyl substitution over other substituents can be explained by the significant production of RSRs following the breaking of the O—CH₃ bond at lower temperatures than occurs for unsubstituted species. The stabilization of these RSRs is enhanced by the vinyl group. These pathways also lead to the formation of unsaturated hydrocarbons susceptible to attack from the radicals formed. Such products are likely to participate in radical-chain reactions leading to repolymerization and, hence, char and tar formation. They may also facilitate secondary-organic aerosol formation during wildfires.

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DATA AVAILABILITY

The data that support the findings of this paper are openly available [105,146]; embargo periods may apply.

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