Thermal Decomposition of Ferulic Acid

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The thermal decomposition of ferulic acid has been studied by thermal gravimetric analysis. The decomposition products were separated by gas-liquid chromatography and identified by GLC retention time and infrared spectral comparison with authentic materials. Combined gas-liquid chromatography–mass spectrometry and thin-layer chromatography were used as supplementary tools in product analysis. Unsubstituted, 4-methyl-, 4-ethyl-, and 4-vinylguaiacols were identified as products from the decomposition of ferulic acid in air and nitrogen atmospheres. Vanillin, acetovanillone (4-hydroxy-3-methoxyacetophenone), and vanillic acid were formed only in the air atmosphere. A mechanism is proposed for a portion of the ferulic acid decomposition.

Hardwood smoke used to cure food products consists of a variety of compounds—carbonyls, acids, and phenols—of which the phenols are claimed to be the major contributors to the characteristic smoky flavor (Husaini and Cooper, 1957; Tilgner *et al.*, 1962). However, the nature of the smoky flavor is still not completely known and the particular phenols involved have not been identified. The phenolic compounds in smoke are reported to be derived from the lignin portion of wood (Bailey, 1947; Tilgner *et al.*, 1962), but, since lignin is such an ill-defined polymer, the mechanism of formation of phenols from lignin is not clear. In a recent study on the chemical composition of wood smoke, the authors reported the identification of a number of phenols, including 4-vinylguaiacol (Fiddler *et al.*, 1966). To confirm the identity of this compound authentic 4-vinylguaiacol was prepared from ferulic acid according to a literature method (Phillips and Goss, 1932). In addition to 4-vinylguaiacol, however, a number of phenols were also found that had been observed in smoke and smoke solutions. These compounds are known to be degradation products of lignin (Phillips and Goss, 1932) and their presence also has been reported in products of lignosulfonate oxidation (Hrutfiord, 1965; Pearl and Beyer, 1954, 1959). Ferulic acid has been found in products of the alkaline oxidation of lignosulfonates (Pearl and Beyer, 1959), alkaline extracts of hardwoods (Fujii and Kurth, 1966; Pearl, 1958), and a variety of grains (Steinke and Paulson, 1964). Its presence in nature is thus well established. However, ferulic acid, either as a primary thermal decomposition product of lignin or in its free state, can be decomposed to 4-vinylguaiacol (Phillips and Goss, 1932; Steinke and Paulson, 1964), which in turn appears to be the source of other phenolic products. This may be a pathway in the formation of these compounds from lignin. This paper describes the thermal decomposition of ferulic acid in the absence and presence of oxygen under controlled heating conditions, the isolation and identification of the resulting degradation products, and their possible mode of formation.

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EXPERIMENTAL AND RESULTS

Materials. Reagent grade samples of chemicals used as standards for the identification of the ferulic acid decomposition products were purchased from commercial sources. The reagent grade ferulic acid was purified by recrystallization three times from water, m.p. 169–70° C. [literature, Phillips and Goss (1932) *trans*-ferulic acid m.p. 171°]. The purity of the ferulic acid was confirmed by thin-layer chromatography under conditions described later.

Thermogravimetric Analysis. An Aminco Thermo-Grav apparatus was used for the thermal stability studies. Approximately 100 mg. of ferulic acid were heated in No. 00000 Coors glazed porcelain crucibles from 20° to 575° C. at a rate of 6° ± 0.3° C. per minute to determine the temperature at which decomposition occurs. Loss of sample weight as a function of time or temperature was recorded on an Electro Instruments X-Y recorder. Dry air or nitrogen was allowed to flow through the system containing the sample at a rate of 10 ml. per minute at atmospheric pressure during the entire run.

The maximum temperature to which the samples were heated was determined from the thermograms of the entire temperature range. In both air and nitrogen atmospheres, the heating was terminated at approximately 320° C. covering the first decomposition stage and 375° C. at the end of the second stage.

When the decomposition products were collected for analyses, approximately 200 mg. of ferulic acid were used. A U-tube containing stainless steel ball bearings was immersed in dry ice–acetone to trap the more volatile products at the exit port of the Thermo-Grav. The higher boiling decomposition products were condensed on the surface of the furnace flask which extended above the furnace. The temperatures here were considerably lower than those at the reaction site.

The contents of the trap, furnace flask, and crucible were dissolved in reagent grade acetone. The combined washings were reduced in volume under a stream of nitrogen then analyzed by gas-liquid chromatography.

Gas-Liquid Chromatography (GLC). Components derived from the thermal decomposition of ferulic acid were separated using a Perkin-Elmer Model 800 dual-column gas chromatograph equipped with a flame ionization detector and fitted with a 4 to 1 ratio stream splitter to permit

peak collection. Two stainless steel columns, 6 feet long by 1/8-inch O.D., packed with 15% Carbowax 20M–terephthalic acid on 60- to 80-mesh Gas Chrom P, were used. The operating conditions were: temperature programming from 70° to 170° C. at 5° per minute with helium carrier gas at a flow of 125 cc. per minute. Injection port and detector temperatures were 210° and 200° C., respectively.

The individual components eluting from the gas chromatographic column were trapped in a capillary tube. The tube was rinsed with approximately 6 μl. of carbon tetrachloride and the solution transferred to a 0.1-mm. path KBr Type D microcavity cell. The infrared spectra were obtained in a Perkin-Elmer Model 421 spectrophotometer fitted with a beam condenser.

Gas-Liquid Chromatography–Mass Spectrometry (GLC-MS). The combined washings of the Thermo-Grav decomposition were also subjected to combined GLC-MS. The gas chromatographic conditions were identical to these described above except that an F and M Model 810 gas chromatograph was used. The mass spectrometer used was a CEC Model 103C.

A stainless steel tee was connected to the exit port of the gas chromatograph. One end of the tee was vented to the atmosphere and the other end was connected to a heated valve manifold so that the analyzer section of the mass spectrometer could be bypassed, when the spectrum of the effluent was not desired. The 4-foot, 0.006-inch I.D. stainless steel capillary tubing connected to the valve manifold acted as a leak to the mass spectrometer, limiting the pressure used from less than 10^{-6} torr to no more than 6.8×10^{-6} torr. All the lines and connections were heated to 225° C. or higher.

Thin-Layer Chromatography (TLC). Thin-layer chromatographic separation and identification of higher boiling components of the Thermo-Grav decomposition products of ferulic acid were achieved by the use of Eastman chromatogram sheets, silica gel Type K301R2.

Two solvent systems were used: 2-butanone–diethylamine–water (6:2:3) and 2-propanol–ammonia–water (8:1:1). The locations of the spots on the developed chromatograms were determined under ultraviolet light, then the plates were sprayed with diazotized sulfanilic acid followed by 4% sodium hydroxide in 50% ethanol (w./v.).

Identification of Components. Gas-liquid chromatograms of the components obtained after the second stage of the decomposition of ferulic acid in the thermogravimetric apparatus either in an atmosphere of air or in an atmosphere of nitrogen are shown in Figure 1. The identifications of the various peaks in each of the atmospheres are listed in Table I. Positive identification of the unknown compounds are claimed only when GLC elution time, infrared spectra, and mass spectra agree with those of the authentic materials. While the unsubstituted, 4-methyl-, and 4-vinylguaiacols are present as a result of the decomposition performed in both air and nitrogen atmospheres, vanillin and acetovanillone appear only in the sample decomposed in air.

The combined GLC-MS technique was used to confirm the identities obtained by GLC retention times and infrared spectroscopy and to obtain further information about peaks 3*a* and 4*a* (Figure 1) in the aerated sample. These

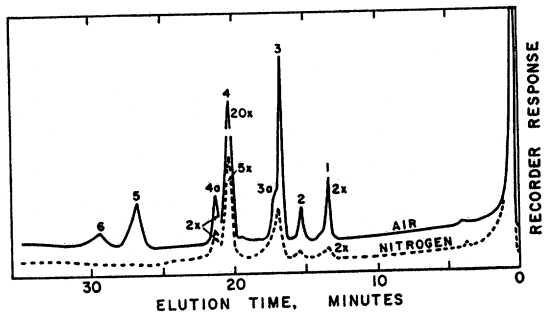


Figure 1. Gas-liquid chromatogram of products derived from thermal decomposition of ferulic acid in an atmosphere of air and nitrogen

peaks could not be separated from the parent peak i sufficient quantity to obtain a good infrared spectrum Peak 3*a*, a shoulder on the side of the 4-ethylguaiac peak (*m/e* 152), had a parent peak of 166. The mo probable molecular formula for this compound is $C_{10}H_{14}O$ A difference in GLC retention time indicated that peak 3 was not 4-propylguaiacol, a possible member of the seri of compounds formed. Peak 4*a*, a shoulder on the sic of the 4-vinylguaiacol peak (*m/e* 150), indicated a pare peak of 172 with the most probable molecular formula $C_{10}H_{12}O_2$. On the basis of GLC retention times, peak 4 was not identical to eugenol, 6-allylguaiacol, or *tran* isoeugenol, compounds having the same given molecul formula. However, the retention times of *cis*-isoeugen and peak 4*a* did coincide. This tentative identificati could not be confirmed, since the high boiling compoun in this region were adsorbed on and slowly desorbed fro the wall of the capillary tubing leading from the gas chr matograph into the mass spectrometer. This resulted complex fragmentation patterns that could not be resolve

While the components in Figure 1 could be read separated by GLC under the conditions described, feru acid, the starting material, and the higher boiling co pounds that also may be products of the reaction w neither detected nor separated. The higher boiling co ponents were separated from the lower boiling compone by thin-layer chromatography. On the basis of the values and the specific color reactions with diazoti sulfanilic acid, vanillic acid was identified only in the a ated sample and the nonreacted ferulic acid was in b samples. The R_f values for these compounds in t different solvent systems are given in Table II.

Thermogravimetric Analysis. Figure 2 shows the wei loss of ferulic acid as the temperature was increased a constant rate. Decomposition started at 200° C. in or in nitrogen. The loss in weight during the first st of decomposition was slightly greater in air (55.0 m than in nitrogen (53.5 mg.). For the second decomp tion stage, which started at 340° C., the loss of weight 34.5 and 23.0 mg. in nitrogen and air, respectively, samples whose initial weights were approximately 100 After the second reaction stage the weight of the resi remained constant in nitrogen, but a very slow decomp tion of the residue continued in air, resulting in the for tion of carbonaceous material.

The maximum rates of decomposition of ferulic for the first stage were 5 mg. per minute in air and 4

Table I. Identities of Components Derived from the Thermal Decomposition of Ferulic Acid

Peak No.	Identity	Reaction Atmosphere: Air	Reaction Atmosphere: Nitrogen	GLC R.T.: Found	GLC R.T.: Std.	IR	MS
1	Guaiacol	+	+	13.5	13.4	+	+
2	4-Methylguaiacol	+	+	15.5	15.4	+	+
3	4-Ethylguaiacol	+	+	17.0	16.8	+	+
3*a*	Unidentified	+	−	17.4			
4	4-Vinylguaiacol	+	+	20.4	20.2	+	+
4*a*	*cis*-Isoeugenol	+	−	21.3	21.4		
5	Vanillin	+	−	26.8	26.6	+	+
6	Acetovanillone	+	−	29.4	29.0	+	+

Table II. R_f Values Obtained by Thin-Layer Chromatography of Components Derived from the Thermal Decomposition of Ferulic Acid

Compound	R_f Values: System I[a]	R_f Values: System II[b]	Color: UV fluorescence	Color: Diazotized sulfanilic acid/NaOH
Ferulic acid				
Standard	0.58	0.37	Blue	Purple
Isolated	0.60	0.39	Blue	Purple
Vanillic acid				
Standard	0.48	0.31	Violet	Orange
Isolated	0.50	0.34	Violet	Orange

[a] 2-Butanone–diethylamine–water (6:2:3).
[b] 2-Propanol–ammonia–water (8:1:1).

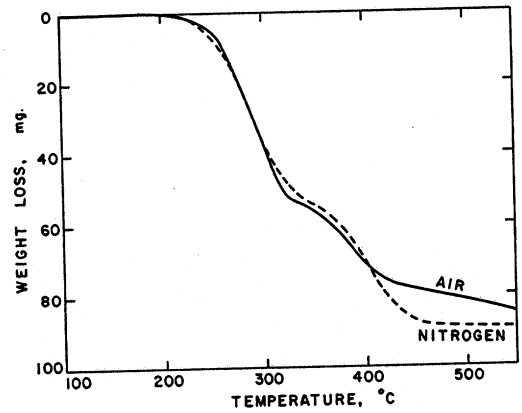


Figure 2. Weight loss of ferulic acid with temperature at a constant rate in an atmosphere of air and nitrogen

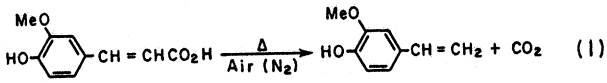
per minute in nitrogen (Figure 3). These maximum rates occurred at 280° C. in each atmosphere. Analyses of the reaction products in both air and nitrogen atmospheres indicated only 4-vinylguaiacol as the major component in this first stage of decomposition.

In the second stage of the reaction, which began at 340° C. in air and 345° C. in nitrogen, the maximum rates of decomposition were 2.1 and 2.5 mg. per minute, respectively. These maximum rates occurred at approximately the same temperature, 380° C. Analysis of the products during the second stage indicated that unsubstituted, 4-methyl-, and 4-ethylguaiacols were formed at the expense of 4-vinylguaiacol in both nitrogen and air atmospheres. The oxygenated products derived from the 4-vinylguaiacol such as vanillin, acetovanillone (4-hydroxy-3-methoxyacetophenone), and vanillic acid were formed only in the air atmosphere.

DISCUSSION

Ferulic acid is an intermediate in the degradation of lignin. Through the combined use of thermogravimetric analysis and gas-liquid chromatography, it has become possible to study the thermal decomposition of ferulic acid and to propose mechanisms of reactions that would account for the end products identified.

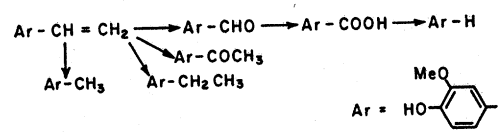
The first stage in the decomposition of ferulic acid occurs at 245° C.; the thermogravimetric analysis curve (Figure 3) shows that the rate of decomposition is greater in the presence of air than in its absence, suggesting that the oxygen in the air acts as a catalyst. Analyses of the reaction products indicated only 4-vinylguaiacol as the major product. Therefore, this first stage must involve the decarboxylation of ferulic acid, Equation 1.



(1)

Since the rate is accelerated by oxygen, the decarboxylation is probably a radical reaction under these experimental conditions.

In the second stage, the oxygen retards the rate, probably because it is a reactant during this phase of the decomposition—that is, the uptake of oxygen by the reactant and the slower loss of the less volatile oxygenated products derived from this reactant apparently decrease the rate of decomposition. Analysis of the products during the second stage also indicated that unsubstituted, 4-methyl-, and 4-ethylguaiacols were formed at the expense of 4-vinylguaiacol in both nitrogen and air atmospheres. The oxygenated products such as vanillin, acetovanillone, and vanillic acid were formed only in the air atmosphere. Since the labile double bond of pure 4-vinylguaiacol is most readily susceptible to air oxidation, it is considered to be the precursor of the oxygenated products. A proposed schematic diagram of these reactions in air is shown in Equation 2.



(2)

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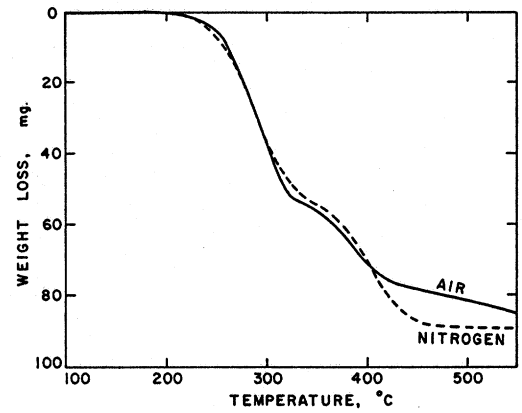

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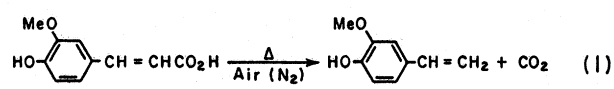

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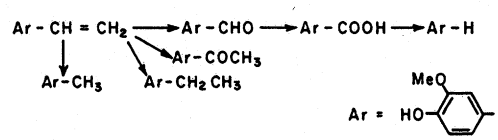

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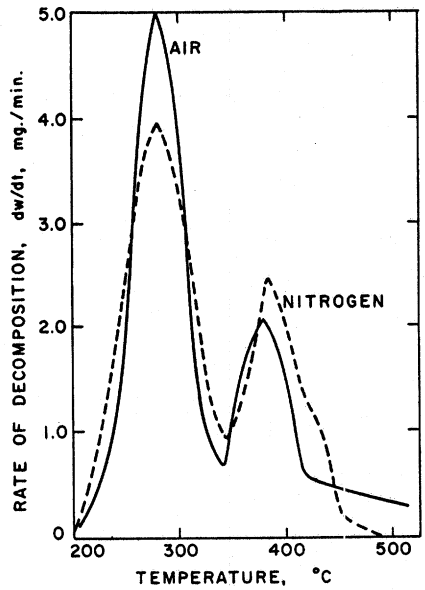

Figure 3. Rate of decomposition of ferulic acid with temperature in an atmosphere of air and nitrogen

The kinetics of decomposition of ferulic acid were evaluated by using the original version of the nonisothermal method (Freeman and Carroll, 1958). The derived equation used was

$$\frac{\dfrac{-E^*\Delta T^{-1}}{2.3\ R}}{\Delta \log W_R} = -X + \frac{\Delta \log dw/dt}{\Delta \log W_R}$$

where E^* = activation energy, R = gas constant, T = absolute temperature, $W_R = w_c - w$, w_c = weight loss at completion of reaction, w = weight loss up to time, t, X = order of reaction, and dw/dt = rate of change of weight with time. Figures 4 and 5 are plots of

$$\frac{\Delta \log dw/dt}{\Delta \log W_R} \ vs. \ \frac{\Delta T^{-1}}{\Delta \log W_R}$$

where the intercept, X, gives the order of reaction and the slope is equal to $-E^*/2.3\ R$. The values for the order of reaction and activation energy are given in Table III.

Since the reactions are three-halves order in air and nitrogen, with the exception of the second stage reaction in air, either radical reactions are taking place (rather than a simple decomposition) or a number of reactions are occurring simultaneously.

The activation energies in the first stage in air (40.3 kcal. per mole) and in nitrogen (32.5 kcal. per mole) suggest that a simple carbon-carbon bond breaking process is not involved, since such a process requires a much greater amount of energy (80 kcal. per mole). The activation energies for the reaction in air are slightly larger than those in nitrogen for both decomposition stages. This could indicate that different mechanisms are operating in the different atmospheres. This has been substantiated by the acceleration of the ferulic acid decomposition in the presence of oxygen and the types of products formed in the air atmosphere. No oxygenated products were isolated in the absence of oxygen, although oxygen is present in the starting material.

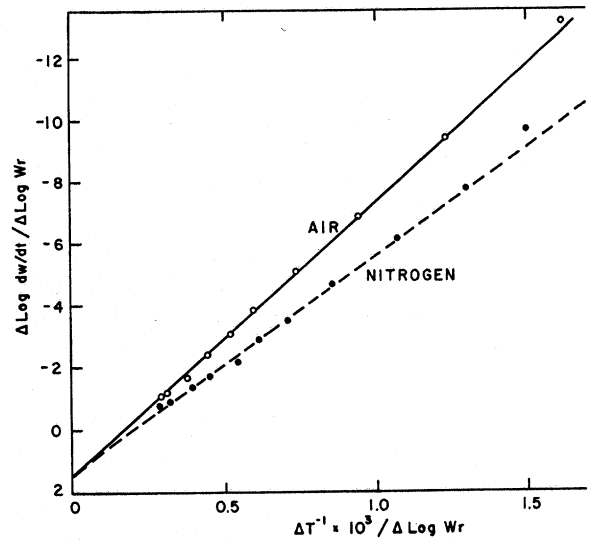

Figure 4. Kinetics of decomposition of ferulic acid during first stage of decomposition in an atmosphere of air and nitrogen

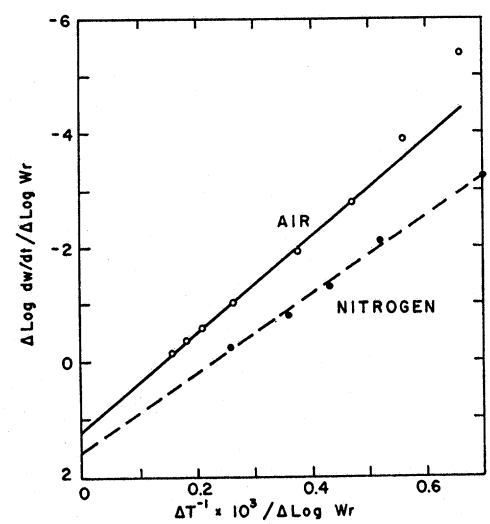

Figure 5. Kinetics of decomposition of ferulic acid during the second stage of decomposition in an atmosphere of air and nitrogen

Table III. Values for the Order of Reaction and Activat Energy for the Thermal Decomposition of Ferulic Aci

	Air	Nitrogen
Order of reaction, X		
1st stage	1.5	1.5
2nd stage	1.2	1.6
Activation energy, E,* kcal./mole		
1st stage	40.3	32.5
2nd stage	38.7	31.3

Usually α,β-unsaturated acids decarboxylate via a cyclic mechanism involving a proton shift (Linstead, 1930). In the case of ferulic acid this proton shift is not possible and the kinetic data showing three-halves order reaction indicates it probably decomposes via a free radical mechanism, if the reaction order is due to only chemical processes. The following mechanism for the first stage, or decarboxylation step, to yield 4-vinylguaiacol is proposed:

Nitrogen atmosphere

$$\mathrm{Ar{-}CH{=}CHCO_2H} \xrightarrow{\mathrm{R}\cdot} \mathrm{Ar{-}CH{=}CHCO_2\cdot} + \mathrm{HR}$$
$$\mathrm{Ar{-}CH{=}CHCO_2\cdot} \rightarrow \mathrm{Ar{-}CH{=}CH\cdot} + \mathrm{CO_2}$$
$$\mathrm{Ar{-}CH{=}CH\cdot} + \mathrm{Ar{-}CH{=}CHCO_2H} \rightarrow \mathrm{Ar{-}CH{=}CH_2} + \mathrm{Ar{-}CH{=}CHCO_2\cdot} \quad (3)$$
$$\mathrm{Ar{-}CH{=}CH\cdot} + \mathrm{HR} \rightarrow \mathrm{Ar{-}CH{=}CH_2} + \mathrm{R\cdot}$$

Air atmosphere

$$\mathrm{Ar{-}CH{=}CHCO_2H} + \mathrm{O_2} \rightarrow \mathrm{Ar{-}CH{=}CHCO_2\cdot} + \cdot\mathrm{OOH}$$
$$\mathrm{Ar{-}CH{=}CHCO_2\cdot} \rightarrow \mathrm{Ar{-}CH{=}CH\cdot} + \mathrm{CO_2}$$
$$\mathrm{Ar{-}CH{=}CH\cdot} + \mathrm{Ar{-}CH{=}CHCO_2H} \rightarrow \mathrm{Ar{-}CH{=}CH_2} + \mathrm{Ar{-}CH{=}CHCO_2\cdot} \quad (4)$$
$$\mathrm{Ar - CH = CH\cdot} + \mathrm{HOO\cdot} \rightarrow \mathrm{Ar - CH = CH_2} + \mathrm{O_2}$$

For the second stage of the thermal decomposition of ferulic acid in nitrogen and air, the number and variety of products from different reactions operating simultaneously make it virtually impossible to propose a single mechanism.

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