Journal of Thermal Analysis, Vol. 2 (1970) 419–428

THERMAL ANALYSIS OF SOME LIGNIN MODEL COMPOUNDS

G. E. DOMBURG, V. N. SERGEEVA and G. A. ZHEIBE

Institute of Wood Chemistry, Academy of Sciences of the Latvian SSR, Riga, U.S.S.R.

(Received May 11, 1970)

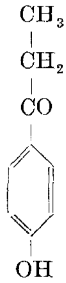
Compounds acting as model biphenyl and phenylcoumarane structural units in the lignin molecule (dehydrodivanillin and dehydrodiisoeugenol) were investigated by thermal analysis. The results were compared with previously obtained data on the thermal degradation of model phenylpropane monomer units of lignin. It was found that the mechanism of thermal degradation of these models and the thermal stabilities of the bonds depend on the structure. The thermal stability of the models increases in the absence of reactive functional groups in the side chain.

The phenylcoumarane unit is relatively stable thermally. The possibility of a free radical mechanism for the thermal degradation is discussed.

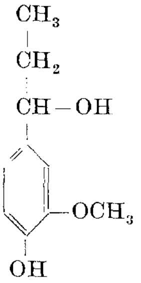
The study of the mechanism of lignin thermolysis is of theoretical and practical significance. Prominence has been given to this question in recent years, especially in connection with the application of DTA to investigate the mechanism and kinetics of degradation.

However, because of the complexity and irregularity of the structure of lignin the interpretation of the thermal curves of this polymeric substance involves great difficulties. The use of model compounds seems to be of importance in solving this problem. The general principles of the thermal degradation of models with structures and functional groups characteristic of lignin fragments, or the intermediates of lignin pyrolysis can be applied to the lignin macromolecule as a whole.

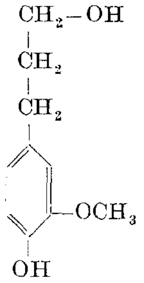
In this paper the recent results [1] obtained with model phenylpropane monomer units of lignin with different side chain structures 1-(4-hydroxyphenyl)propanone-1 **(I)**, 1-(4-hydroxy-3-methoxyphenyl)propanol-1 **(II)**, 1-(4-hydroxy-3-methoxy-phenyl)propanol-3 **(III)** and 1-(4-hydroxy-3-methoxy-phenyl)propen-1--ol-3 **(IV)** are discussed. This information is compared with the data on the kinetics of the thermal degradation of the model biphenyl and phenylcoumarane structural units in lignin [dehydrodivanillin **(V)** and dehydrodiisoeugenol **(VI)**].



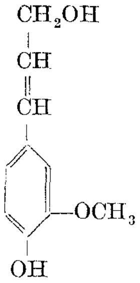
I



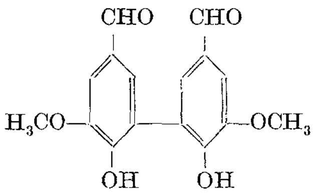
II



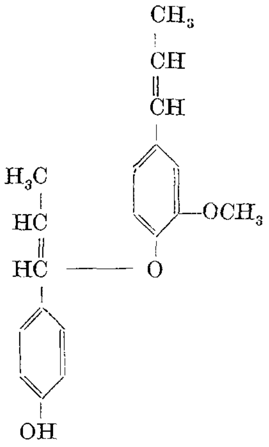
III



IV



V



VI

Experimental

Measurements were carried out with a Paulik – Paulik – Erdey derivatograph. The heating rate was 12°/min up to 600°, and the weight of sample was 200 mg. Crucibles containing sample and reference (Al_2O_3) were covered with a lid; the vapour – gas mixture was not exhausted. The thermal treatment of a preparation was performed in a muffle in which samples in closed glass tubes were heated at the same rate as in the derivatograph.

The kinetic parameters were calculated from the measurement by the Freeman – Carrol [2] method. IR spectra were taken of the samples in the form of KBr pellets with a UR – 20 Zeiss spectrophotometer. The calculation of concentration of paramagnetic centres (PMC) was made from electron paramagnetic resonance (EPR) spectra taken with an RE – 1301 radiospectrometer directly during heating using diphenylpicrylhydrazyl as standard, and from thermal data [3].

Discussion

Earlier investigations [1] have shown that during the thermal degradation of 1-(4-hydroxyphenyl)propanone-1 (I) volatile products can be observed at about 210° and the main process of decomposition begins at 260°, reaching its maximum rate at 325° (Fig. 1). In the temperature range 260° to 325° the rate constant for the reaction increases 54-fold and over 70% of **I** decomposes. The degradation reaction of **I** follows pseudo-first order kinetics. The endothermic peak at 325°

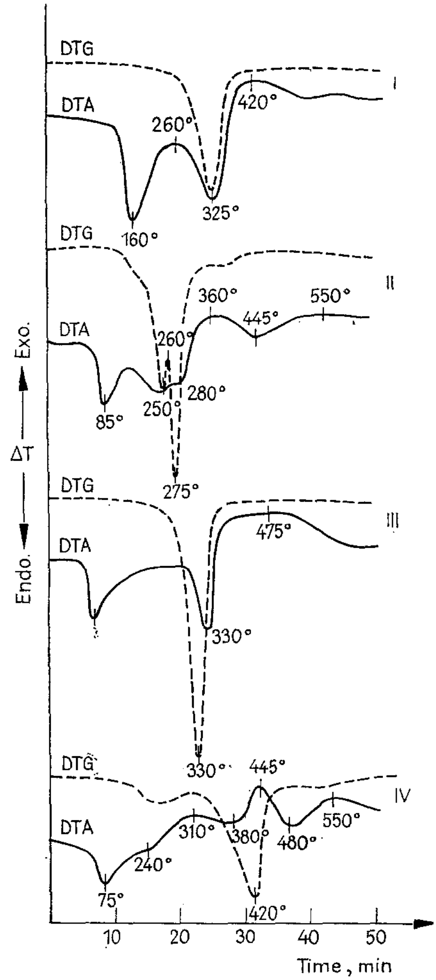


Fig. 1. DTG and DTA curves of phenylpropane monomers. I. 1-(4-hydroxyphenyl)propanol-1; II. 1-(4-hydroxy-3-methoxyphenyl)propanol-1; III. 1-(4-hydroxy-3-methoxyphenyl)propanol-3; IV. 1-(4-hydroxy-3-methoxyphenyl)propen-1-ol-3

corresponds to the completion of $C-C$ bond breaking in the propyl side chain. The initial degradation of **I** to radicals $HO-$$-\dot{C}O$ and $CH_3-\dot{C}H_2$ seems to be most probable energetically although simultaneous $C_{aryl}-C_{alkyl}$ bond breaking is not excluded.

The degradation rate of **I** slows down above 325° and decomposition is practically complete at 370°.

The thermal degradation of 1-(4-hydroxy-3-methoxyphenyl)propanol-1 **(II)** (Fig. 1) is a multistep process which starts at about 160°. The maximum degradation rate of the first stage is at 250°. Within this temperature range the rate constant of the loss of weight increases 29-fold and **II** loses over 40% of its weight (Table 1).

Table 1

Kinetic parameters of the decomposition of model compounds

Compound	Temperature range °C	Weight loss %	Degradation rate constant (C.10⁴)		Activation energy E kcal/mole
			C_{init}	C_{fin}	
I	260—325	72.2	2.6	140.0	33.36
	325—370	14.1	140.0	34.0	15.62
II	160—260	42.0	0.7	20.2	15.08
	260—280	19.7	20.2	71.0	37.00
	280—340	9.6	71.0	13.0	20.62
III	250—370	94.0	1.5	210.0	33.36
IV	180—260	7.5	2.6	5.2	5.25
	260—300	3.3	5.2	3.2	9.14
	300—440	46.1	3.2	27.0	27.45
V	285—325	12.8	1.2	24.0	60.78
	325—380	14.5	24.0	5.4	24.58
	380—600	50.2	5.4	69.6	37.47
VI	370—405	29.0	10.4	63.0	45.70
	405—445	11.0	63.0	17.0	30.16

The apparent activation energy is comparatively low.

Intramolecular and intermolecular dehydration reactions of the benzyl alcoholic groups occur during the first stage of the process. It seems that some molecules of **II** form unsaturated compounds which are removed. The remaining molecules form dimers and more complex structures which remain in the solid phase.

$C-C$ bond breaking between the α- and β-carbons in the propyl side chain and between the benzene nucleus and the side chain occurs in the second stage of the process at the fairly low temperature of about 275°. (The activation energy increases 2.5-fold.)

The picture of the thermal degradation of 1-(4-hydroxy-4-methoxyphenyl)propanol-3 **(III)** is very similar to that of **I** (Fig. 1). Above 250° the rate of degradation of **III** (which proceeds according to a first order rate equation) increases significantly and reaches a maximum at about 330°, when C–C bond breaking in the propyl side chain is completed. Decomposition is practically complete by 370° (Table 2). The total activation energy of decomposition amounts to 33.36 kcal/mole, which agrees well with the data for **I**.

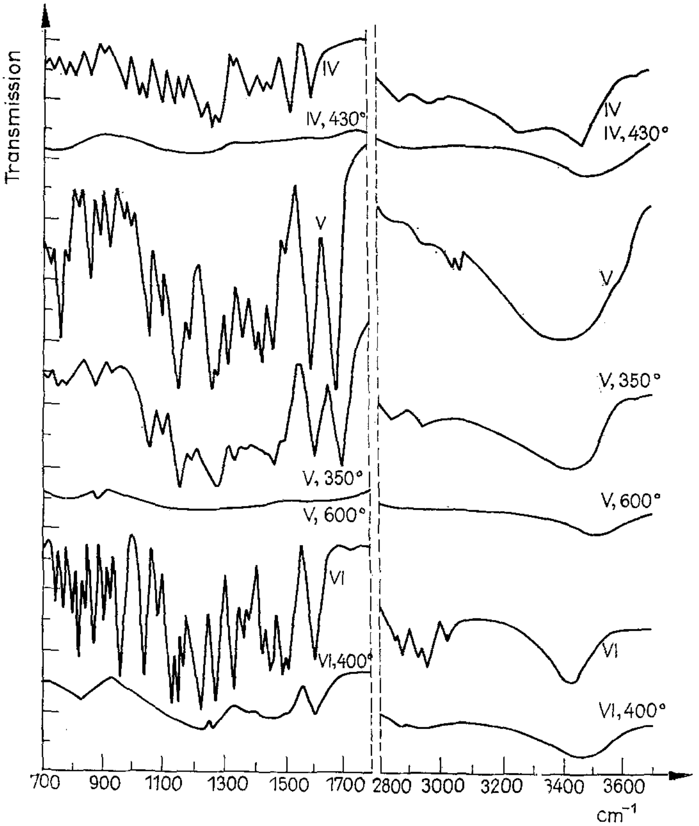


Fig. 2. IR spectra of 1-(4-hydroxy-3-methoxyphenyl)propen-1-ol-3 (**IV**), dehydrodivanillin (**V**) and dehydrodiisoeugenol (**VI**) before and after thermal treatment up to the given temperatures

The thermal degradation of 1-(4-hydroxy-3-methoxyphenyl)propen-1-ol-3 is more complicated, as seen from the thermal curves (Fig. 1). The process involves three basic stages beginning at 160° as for **II**. In the first stage, at 200°–300°, intermolecular condensation-polymerization reactions take place. Only about 11 % of the initial weight is involved in decomposition. The process occurs without a marked heat absorption, and has a small activation energy (Table 1).

During the second stage decomposition proceeds with maximum rate at 420°, the total activation energy increasing about 2-fold. The endothermic peak at about

380° appears to conform principally with breaking of the C – C bond in the side chain in the α-position to the double bond, and of bonds newly formed in the first stage. Degradation takes place according to a free-radical mechanism and finishes with a strongly exothermic step (440°).

It can be seen from the IR spectra in Fig. 2 that in the product of heat treatment of **IV** up to 430° the initial guaiacyl structure has been completely destroyed; the spectrum is diffuse, and typical of carbonaceous material.

In the third stage of degradation some rearrangement of the system occurs (endothermic peak at 480°), but without a significant isolation of volatile degradation products.

Dehydrodivanillin (V)

Two endothermic processes take place during the thermal treatment of this dimer, as seen from Fig. 3. The first process starts at about 300° with a DTA maximum at 305°; the second one reaches its maximum at 380°. The isolation of volatile products (maximum rate at 325°) indicates that after melting in the first endothermic stage **V** decomposes. To elucidate the nature of this reaction the thermal treatment of **V** was carried out up to 350° and the reaction products were investigated. A crystalline substance of m.p. 83° was isolated from the volatile products and identified as vanillin. Its yield was calculated from the methoxy group loss and amounted to 12%. (It has been established that under thermal treatment up to 350° the methoxy groups of vanillin do not split off.) This corresponded to the weight loss of **V** in the temperature range 300° – 350°.

Vanillin formation from **V** is possible only by C – C bond breaking between guaiacyl units, and therefore the temperature of this bond breaking is about 300°.

It has been calculated that degradation of **V** in the temperature range 285° – 325° proceeds with a considerable increase in reaction rate constant (Table 1). The total value of the apparent activation energy in this temperature range is 60.78 kcal/mole. Although the data given in the literature for the energy of C – C bond breaking in diphenyl are well over this value, from 93.7 to 103.0 kcal/mole [4, 5], it should be borne in mind that the activation energy is determined both by the bond breaking energy and the energy of bond formation. In addition the decrease in value of the apparent activation energy can be affected by the presence of some energetically similar bond type in the molecule or by recombination reactions. This fact seems to explain the low values of activation energy of the thermal degradation of lignin [6 – 9]. The activation energy of destruction of even the structurally rather simple polymolecule of phenol resin with the bond type $C_{aryl} - C_{alkyl} - C_{aryl}$ is not higher than 18 kcal/mole in the temperature range studied [10].

Thus the value of 60.78 kcal/mole is comparatively high and indicates the uniformity of the bonds which are broken.

During heating the EPR signal increases. The PMC concentration of the solid phase reaches 4.0×10^{19} spin/g at 300° – 320°, compared with about 10^{17} at the start (**V**). Considering all these facts one can reasonably suggest that biphenyl bond degradation takes place according to a free radical mechanism. A part of the free radicals formed in the first stage of the process are blocked by hydrogen forming vanillin. However, most radicals are involved in different recombination reactions. This is followed by a decrease of degradation rate above 325°. The value of activation energy drops in the second stage of the process.

Judging from the elementary composition and methoxy group content (Table 3) the intermediate solid product formed during the thermal treatment of **V** up to 350° does not greatly differ from the initial compound. However, the intensities of all the bands of the IR absorption spectrum of this product decrease significantly (Fig. 2), especially in the region of the phenolic hydroxyl absorption 3200 – 3400 cm^{-1} : O – H vibrations, including intermolecular hydrogen bonds 1255 cm^{-1} : aromatic ring vibrations and C – O vibrations around 700 – 1000 cm^{-1}, a region characteristic of out-of-plane vibrations of unsubstituted aromatic hydrogen atoms. Consequently, structural rearrangement involving condensation must have taken place.

The intermediate formed becomes unstable at about 380° and in the third stage of the process **V** loses a further 50.2 % of its weight. The degradation rate constant increases 13-fold in this case and the activation energy rises. After thermal treatment up to 600° the final product (17.9 % of initial weight of **V**) is carbonaceous material with a PMC concentration of 4.0×10^{20} spin/g, and its IR spectrum has a completely diffuse nature (Fig. 2).

Dehydrodiisoeugenol (VI)

The thermal decomposition of **VI** starts at 350° and proceeds with two endothermic effects (Table 2, Fig. 3). Weight loss amounts to only 11.0 % up to 370°. The higher activation energy value (Table 1) corresponds to the endothermic effect at 390° – 400°. Within this temperature range the PMC concentration is

Table 2

Relative thermal stabilities of model compounds

Compound	Temperature at the start of weight change °C	Temperature of the maximum rate of weight loss °C	Complete destruction	
			Temperature °C	Residue %
I	210	325	370	10.0
II	160	250; 275	425	16.5
III	220	330	370	8.0
IV	160	(240); 420	600	34.0
V	280	325; (500)	600	22.5
VI	350	405; (540)	600	12.0

one order higher than that measured during thermal treatment at 300°. In the IR spectrum of the product of thermal treatment of **VI** up to 400° (Fig. 2) several absorption bands are absent. These are due to the vibrations of the benzene ring in the coumarane units (1495 cm^{-1}), and to ethylene group vibrations (905, 960 cm^{-1}). In the region of phenolic hydroxyl vibrations (1030, 1220, 3430 cm^{-1}), decrease of absorption takes place. Judging from these variations of the spectrum one can see that in the temperature range 390–400° destruction of the phenylcoumarane structure takes place with C–C bond rupture in the chains in the phenylpropane units. This is characteristic of the double bond in the side chain. (cf. **VI**).

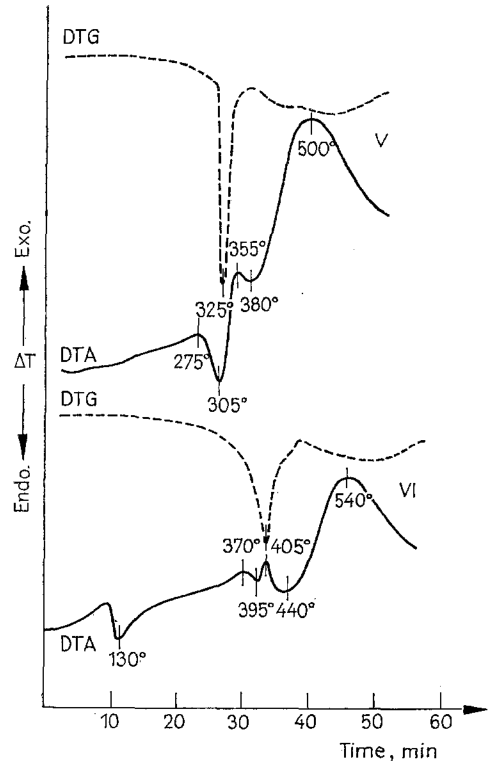


Fig. 3. DTG and DTA curves of dehydrodivanillin (V) and dehydrodiisoeugenol (VI)

The endothermic peak at 405° characterizes a recombination of free radicals into an unstable intermediate which still contains one methoxy group per 3 conventional phenylpropane units (Table 3). Degradation of this system at 450° is followed by the increase of PMC concentration to about 10^{20} spin/g at 500°.

Thus the mechanism of the thermal degradation of model phenylpropane compounds of lignin type is dependent on their structures. Monomer compounds

Table 3

Change in the elemental composition of model compounds after thermal treatment

Compound	Temperature °C	Elemental composition %			Methoxy group content %
		C	H	O	
IV	20	60.22	6.66	33.12	17.22
	430	80.13	4.23	15.64	2.58
	600	—	2.80	—	0.26
V	20	63.50	4.60	31.90	20.53
	350	67.19	4.08	28.73	18.08
	600	74.45	2.29	23.26	0.15
VI	20	73.60	6.80	19.60	19.00
	400	78.40	5.22	16.38	7.58

without reactive groups or multiple bonds in the side chain undergo the basic degradation in one clear-cut endothermic process at 325°—330° with C—C bond breaking in the side chain. These compounds decompose almost completely by 370°. The absence of reactive functional groups in the side chains of dehydrodiisoeugenol and the presence of the phenylcoumarane unit in its structure give rise to an increased initial thermal stability of dehydrodiisoeugenol. The compounds containing OH groups in the side chain in the α-position to the aromatic nucleus or double bonds with a conjugated OH group decompose slowly in several stages. Such compounds have a lower initial thermal stability (by 50°—60°), but a higher thermal stability of intermediate structures. The decrease of the initial thermal stability is due to the primary dehydration, condensation and polymerisation reactions brought about by the active groups in the side chains. The presence of an α-OH group gives rise to C—C bond breaking in the side chain at 275°. In the presence of double bonds this process takes place at considerably higher temperatures (380°—400°).

C—C bond breaking between two guaiacyl units without propane chains takes place at 300°—310° and is characterized by high values of the degradation rate constant and activation energy. C—C bond breaking in the investigated compounds proceeds by a free radical mechanism.

References

1. G. E. Domburg, V. N. Sergeeva and G. A. Zheibe, Khimiya drevesiny (in the press).
2. E. S. Freeman and B. Carrol, J. Phys. Chem., 62 (1958) 394.
3. G. E. Domburg, V. N. Sergeeva, M. Koshik and L. J. Salna, Izv. AN Latv. SSR, Ser. Khim., 4 (1968) 497.
4. M. Szwarc, Chem. Rev., 47 (1950) 75.
5. N. N. Semenov, O nekotorykh problemakh Khimicheskoi kinetiki i reaktsionni sposobnosti, Moscow, 1958, p. 30.

6. M. Koshik, L. Geratova, F. Rendosh and R. Domansky, Holzforsch. und Holzverwertung, 20 (1968) 15.
7. B. Solomon, G. Rozmarin, A. Biro and Gr. Simionesku, Cellul. Chem. Technol. 1 (1967) 601.
8. A. J. Stamm, Ind. Eng. Chem., 48 (1956) 413.
9. G. E. Domburg, V. N. Sergeeva and A. N. Popov, Khimiya drevesiny, 6 (1970) 133.
10. S. Madorskii, Termicheskoe razlozhenie organicheskikh polimerov, Izdatelstvo Inostrannoi literaturi, Moscow, 1966, p. 307.

Résumé — Étude thermique de composés modèles pour les liaisons structurales de type diphényle et phénylcoumaranne dans la molécule de lignine (déhydrodivanilline et déhydrodiisoeugénol). Comparaison des résultats avec ceux obtenus précédemment dans le cas de la dégradation thermique de composés servant de modèles pour les unités monomères de phénylpropane dans la lignine. Détermination du mécanisme de la dégradation thermique de ces modèles et de la stabilité thermique des liaisons suivant la structure. La stabilité thermique augmente en l'absence de groupes fonctionnels réactifs dans la chaîne latérale. La liaison de type phénylcoumaranne est thermiquement la plus stable. On suppose un mécanisme avec radical libre pour la rupture des liaisons structurales.

Zusammenfassung — Modellverbindungen mit Biphenyl und Phenylcumaran Bindungen im Lignin wie Dehydrodivanillin und Dehydrodiisoeugenol wurden einer thermoanalytischen Prüfung unterworfen und die Ergebnisse mit jenen der thermischen Zersetzung von Phenylpropan-monomeren Modellen des Lignins verglichen. Es wurde festgestellt, daß der Mechanismus der thermischen Zersetzung und die thermische Stabilität der Bindungen strukturabhängig sind. Die thermische Stabilität der Modelle nahm mit Abwesenheit reaktionsfähiger funktioneller Gruppen an der Seitenkette ab. Die Bindung vom Typ des Phenylcumarans ist thermisch am stabilsten. Das Zerreissen der Bindungen scheint durch einen Mechanismus durch freie Radikale zu erfolgen.

Резюме — Проведено термографическое исследование соединений, моделирующих дифенильный и фенилкумарановый типы структурных связей в молекуле лигнина (дегидродиванилин и дегидродиизоэвгенол). Результаты сопоставлены с полученными ранее данными по терморастаду моделей фенилпропановых мономерных единиц лигнина. Показано, что механизм термического разложения моделей и термоустойчивость С—С связей зависят от типа связи между мономерами и от структуры боковой цепочки модели. Отсутствие реакционноспособных функциональных групп в боковой цепи повышает термостабильность модели. Фенилкумарановый тип связи является наиболее термически устойчивым. Высказано мнение о свободно-радикальном механизме разрыва структурных связей исследованных соединений в условиях эксперимента.