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THERMOCATALYTIC TRANSFORMATIONS OF LIGNIN MODEL COMPOUNDS

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ABSTRACT

By applying TA, GLC and mass-spectrometry, the influence of phosphoric acid on the mechanism of thermal degradation of lignin dimeric model compounds was studied. It was established that phosphoric acid catalyzed the intermolecular dehydration reactions resulting in the advantage formation of carbon or ether bonds depending on the activity of the hydroxyl groups of the propane side chain.

INTRODUCTION

The investigation of the thermal transformations of wood and its components in the presence of fire retarding and coal formation promoting compounds has the aim to reveal their action mechanism at the separate stages of the process. To establish the influence of phosphoric acid on thermal stability of lignin basic structure bonds and functional groups, the dimeric model compounds with β-ether bonds were investigated.

MEASURING METHODS

1-(3-methoxy-4-oxyphenyl)-2-(2-methoxyphenoxy)-propanol-1 (I) and 1-(3-methoxy-4oxyphenyl)-2-(2-methoxyphenoxy)-3-oxypropanone-1 (II) were used. Phosphoric acid (5% from the sample mass) was introduced as aqueous solution at room temperature. The thermal treatment of the preparations was carried out isothermally at 400°C. Chromato-mass-spectrometric analysis was performed on the apparatus "MAT-III", GLC - on the chromatograph "Chrom-5" (stationary phase 5% SE-30, 120 $\xrightarrow{4^{\circ}/\mathrm{min}}$ 300°C, length of column - 2 m). Thermal analysis was performed using a derivatograph "MOM" (the temperature range 20-500°C, the heating rate 5°/min, nitrogen flow 60 ml/min).

RESULTS AND DISCUSSION

The β-guaicyl ether I, containing a high reactivity benzyl alcohol group, at initial stage of the thermal treatment, active-

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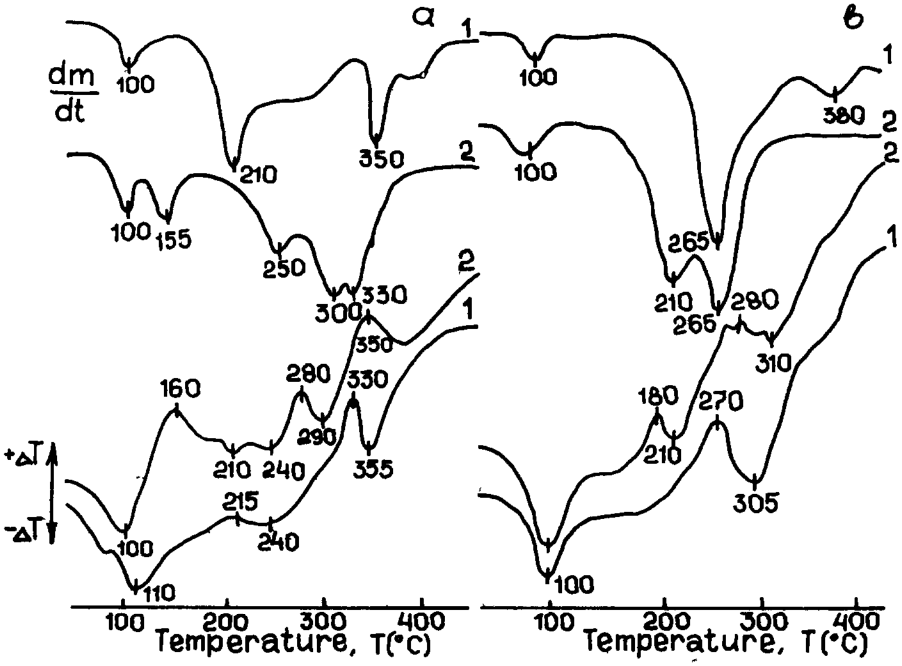

Fig. 1. DTG- and DTA-curves for ether I (a) and ether II (b); 1 - neat compounds, 2 - compounds containing H_3PO_4.

ly developes the dehydration reactions (Fig. 1a, T_{max} 210°C), leading to the formation of intermediate product of condensation (ref.1). At the higher temperatures, C-O-C- and low-stable C-C- bonds are spliting, and volatile products are formed; their summary yield at 500°C is 78.2%. The maximal yields have guaiacol, formation of which is determined by both the cleavage of β-ether bond and C_{aryl}- C_{alk}- bond, and monomers with the double bonds in the side chain, being the products of intramolecular dehydration reactions (Fig. 2). The detection of compound M 222, the possible product of destruction of tetramer with α-ether bond (ref.2), indicates that intermolecular reactions also take place.

In the presence of phosphoric acid, dehydration reactions of the ether I proceed with maximal rate at 155°C (Fig. 1a). The major amount of volatile destruction products is isolated at 250 and 300°C. The number of forming compounds decreased, but their summary yield, at 500°C, fell by 11.2%, that indicates more selective direction of thermal destruction. The yields of guaiacol and guaiacylpropanone-2 increase as a result of catalytic destruction of C_{aryl}- C_{alk}- and C-O-bonds. But α-carbonyl compounds and monomeric products of intramolecular dehydration do not form. However, to a certain extent, this process takes place, judging from the formation of compound M 286 having structure of 1-(3-methoxy-4-oxyphenyl)-2-(2-methoxyphenoxy)-propene-1,2 (Fig. 2).

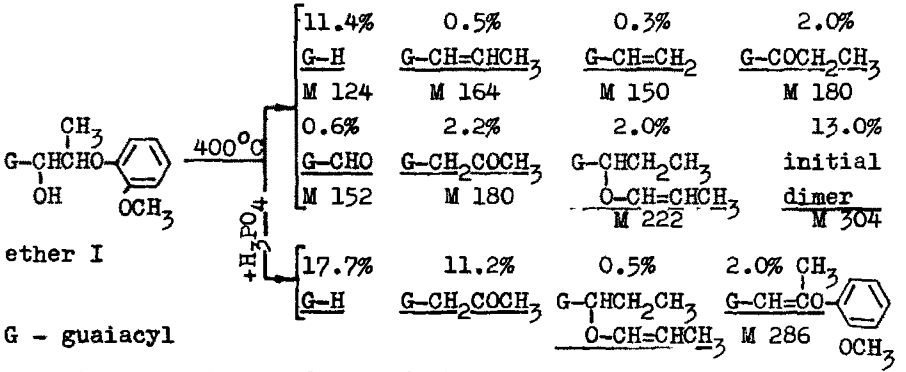

Fig. 2. The major products of thermal degradation of ether I.

Earlier (ref.3), on the monomeric model 1-(3-methoxy-4-oxyphenyl)-propanol-1, we had shown that in the presence of phosphoric acid, the benzyl alcohol group takes part in the formation of unstable dimeric α-ether, reconstructing in thermally stable dimer with C-C-bonds - diisoeugenol. A low yield of the compound with M 222 and higher thermal stability of intermediate structure, obviously, confirms the analogous way of transformation of benzyl alcohol group of the ether I in the presence of phosphoric acid.

The thermal destruction of the ether II, containing γ-hydroxyl, proceeds at elevated temperatures (Fig. 1b). The dehydration reactions develope in the basic degradation stage (T_{max}265°C). The total amount of volatile compounds, among them the major are guaiacol, monomeric products of intramolecular dehydration and α-carbonyl compounds, is 72,7%, up to 500°C (Fig. 3).

In the presence of phosphoric acid, the TA-curves of the ether II fix the low-temperature development of the primary condensation reactions, accompanied by an isolation of water (Fig. 1b, DTA-curve - T_{max} 180°C, DTG-curve - 210°C). The total amount of volatile compounds increases up to 75,5%. Parallely with guaiacol, whose yield almost unchanged, the major product of the ether II destruction is the compound with M 194, identified as the guaiacyl-2,3-epoxypropanone-1. This compound, as well as the compound with M 208, is formed, probably, via the intermediate dehydration stage, resulting in the formation of intermediate γ-ether.

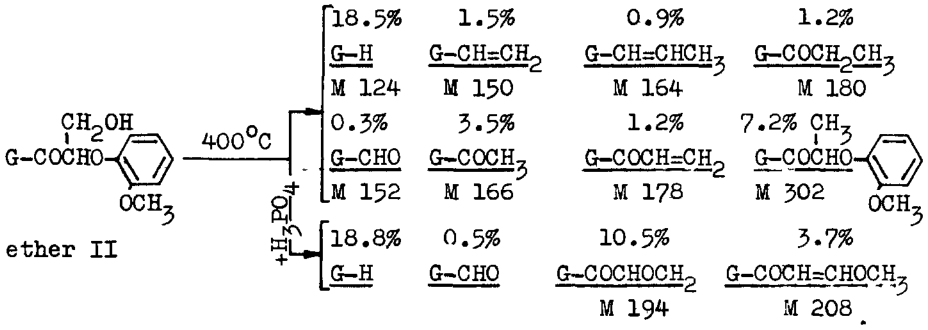

Fig. 3. The major products of thermal degradation of ether II.

The carbonyl group of the ether II is thermostable and does not undergo the influence of the phosphoric acid.

CONCLUSIONS

At the destruction of 1-(3-methoxy-4-oxyphenyl)-2-(2-methoxyphenoxy)-propanol-1, phosphoric acid catalyzes the intermolecular reactions of dehydration, resulting in a formation of unstable α-ethers, reconstructing in diisoeugenol structures. As a result of thermocatalytic degradation of 1-(3-methoxy-4-oxyphenyl)-2-(2-methoxyphenoxy)-3-oxypropanone-1, products of intermolecular condensation with stable γ-ether bonds generally are formed.

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