

Thermal transformations of biologically active derivatives of cinnamic acid by TPD MS investigation

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ABSTRACT

Pyrolysis of biologically active cinnamic acid derivatives: cinnamic, coumaric, ferulic and caffeic acids was studied by the method of thermal programmed desorption mass spectrometry. It was found that pyrolysis of coumaric and caffeic acid proceeds as a thermal decarboxylation reaction of the first order. Kinetic parameters of the reaction of decarboxylation including its order, the activation energy and pre-exponential factor were calculated. Under conditions of TPD MS experiment cinnamic acid sublimates at temperatures above 200 °C. Thermal decomposition of ferulic acid proceeds in several stages.

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1. Introduction

Ferulic acid (FA) is widely spread in nature. FA is a product of lignin biotransformation and therefore it exists in relatively large amounts in river waters [1], seawaters [2], and in various soils [3]. It plays an important role in the processes of humification, participates in the binding and biotransformation of xenobiotics present in the environment and, especially, in humus. This pollutant includes many agricultural and industrial chemicals and their degradation products, as well as naturally occurring substances [4]. At the same time there is no common viewpoint on the biosynthesis and biodegradation processes of the lignin itself [5–7]. Ferulic, coumaric, sinapic acids and their corresponding phenolic alcohols (coniferyl, coumaric, sinapic) are intermediate elements both in the lignin synthesis [7] and in its biodegradation up to humic acids. Therefore, ferulic and coumaric acids can be used in model studies as active compounds involved in the formation of plant cell polymeric structures, as well as samples of the humus components. Study of kinetics and thermal decomposition mechanisms of a number of phenolic acids can define the connection between the acid structure specifically, the presence of substituents ($-\text{OCH}_3$, $-\text{OH}$) in the aromatic ring and acid reactivity. Particularly, this is important for better understanding the biosynthesis and biodegradation processes of lignin and the fer-

uloyl residue significant role in controlling cell wall extensibility [8–10].

Numerous publications are devoted to cinnamic acid and its derivatives being active compounds of herbal medicines [11,12]. Aromatic hydroxycarboxylic acids have high antioxidant and metal ion chelating capacity and demonstrate various biological and biochemical effects including desensitizing, immunomodulatory, antirheumatic and other properties. They exhibit choleric, hypolipidemic, hypocholesterolemic, antibacterial, anticoagulant effects, and reduce the toxicity of anticancer drugs [11–15]. To produce dosage forms based on medicinal herbs, stability of active compounds has to be studied first. Therefore, the investigation of stability of the aromatic hydroxycarboxylic acids, in particular, using the thermal programmed desorption mass spectrometry (TPD-MS) method is of great practical importance. In addition, cinnamic acid derivatives are widely used as matrices in Matrix-assisted laser desorption and ionization mass spectrometry (MALDI MS) [16]. Thus, a detailed study of the mechanisms of thermal reactions of cinnamic acid derivatives using the TPD-MS method may be useful to establish the ionization mechanisms in MALDI MS.

In the previous works [17,18] we have reported the TPD MS study of the cinnamic and ferulic acid interaction with fumed silica. Several decomposition pathways of these acids on silica surface were found. These were reactions of decarboxylation, dehydration followed by ketene formation and the reaction of the formation of the corresponding arylacetylene. In view of this fact it was interesting to determine whether the same reactions would be observed during the thermal decomposition of cinnamic acids in the condensed state. The transient methods, in particular, TPD MS are extensively applied to study kinetics and mechanism of pyrolysis

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and heterogeneous catalytic processes [19–25]. MS thermograms can be used to determine various desorption kinetic parameters including the order of the reaction, the pre-exponential factor, desorption activation energy, and activation entropy. In this paper we have studied the thermal stability of a number of cinnamic acid derivatives, and determined kinetic parameters of their pyrolysis.

2. Experimental

2.1. Reagents

Cinnamic, coumaric, caffeic and ferulic acids were purchased from Sigma and used without previous purification.

2.2. Mass spectrometry

The TPD MS experiments were performed on a MX-7304A monopole mass spectrometer (Sumy, Ukraine) with electron impact ionization adapted for thermodesorption measurements as described earlier [17,18]. A typical TPD MS test comprised placing the samples of 0.1–2 mg weight on the bottom of a molybdenum-quartz ampoule, its evacuating to $\sim 5 \times 10^{-5}$ Pa at $\sim 20^\circ\text{C}$ and the sample heating at a rate of 0.15°C/s up to $\sim 750^\circ\text{C}$. The volatile pyrolysis products passed through a high-vacuum valve into the ionization chamber of the mass spectrometer, where they were ionized and fragmented by electron impact. After mass separation in the mass analyzer, the ion current due to desorption and pyrolysis products were recorded with a secondary-electron multiplier VEU-6. The mass spectra were recorded (within 1–210 Da) and analyzed using a computer-based data acquisition and processing setup. During each TPD MS experiment, ~ 240 mass spectra were recorded. In the course of a thermodesorption experiment, the sample was heated sufficiently slowly while the rate of evacuation of the volatile pyrolysis products was high. Therefore, the diffusion effects could be neglected and the intensity of the ion current could be considered proportional to the desorption rate. This enabled the calculation of the non-isothermal kinetic parameters.

The non-isothermal parameters of desorption (thermal decomposition) and chemical reactions in the condensed phase and on silica surface were calculated using the personally designed computer program. This program enables the calculation of various non-isothermal kinetic parameters of the reactions in the condensed phase and on the surface of highly dispersed oxides, such as the order of the reaction (n), the pre-exponential factor (k_0), activation energy (E^\ddagger), and activation entropy (dS^\ddagger) from TPD MS data. The non-isothermal parameters were calculated only for well-resolved peaks, the peaks for which the form and position on the temperature scale were reproduced in several experiments.

3. Results and discussion

The TPD MS study has shown that when heated in vacuum in the absence of oxygen cinnamic acid is sublimated at a temperature above 200°C . In this case, cinnamic acid molecular ion with a mass of 148 Da and its fragments, which are formed in the ion source of the mass spectrometer by electron impact are observed (Fig. 1).

Coumaric acid, which in contrast to cinnamic acid has a hydroxyl group in para-position, demonstrates the radically different pyrolysis mechanisms. It is realized as a reaction of decarboxylation at $T > 70^\circ\text{C}$. In this case, in mass spectra (Fig. 2a) the products of decarboxylation are observed, such as carbon dioxide (44 Da), corresponding vinylbenzene (120 Da), and its fragment ions formed in the ion source of the mass spectrometer by electron impact. It should be noted that at the temperature range $25\text{--}750^\circ\text{C}$ the molecular ion 164 Da is absent. The largest mass observed in mass

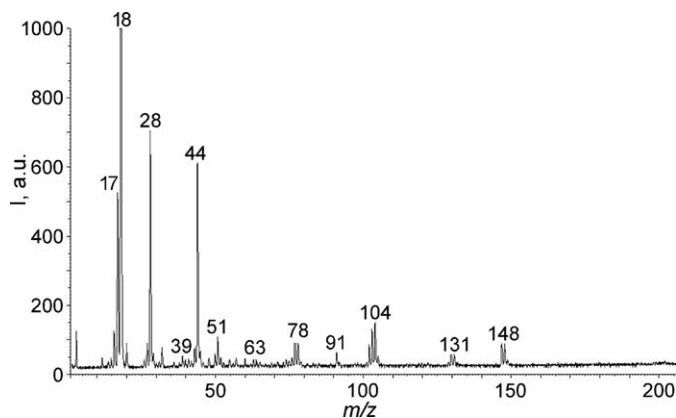


Fig. 1. Mass spectrum obtained for cinnamic acid sublimation at 200°C .

spectra is an ion of m/z 120. The shape of thermograms for m/z 44 and m/z 120 (Fig. 2b) is typical for the processes of the first order [26]. Mathematical processing of these thermograms gave kinetic parameters of the decarboxylation reaction of coumaric acid (Table 1). Negative values of dS^\ddagger indicate the presence of the highly ordered transient state. This testifies that decarboxylation proceeds as a thermal reaction of β -elimination via a cyclic transient state. Common feature of such reactions is the intramolecular hydrogen transfer via the cyclic transient state. Cyclic structure of the transition state in such reactions requires the elimination to

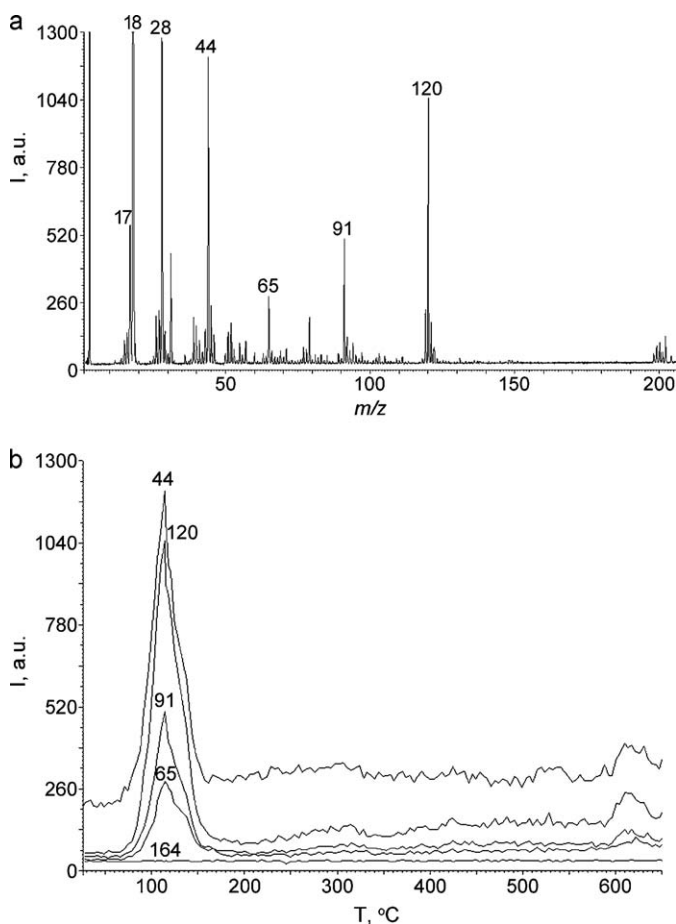


Fig. 2. Thermal decomposition of coumaric acid in the condensed state: (a) mass spectrum at $110\text{--}115^\circ\text{C}$; (b) thermograms of the coumaric acid molecular ion of (m/z 164), CO_2 molecular ion (m/z 44), molecular ion of 4-hydroxy-phenylethylene (m/z 120) and its daughter ions (m/z 65, 91).

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