

NON-ISOTHERMAL DECOMPOSITION OF BIOMOLECULES STUDIED BY MEANS OF TEMPERATURE-PROGRAMMED DESORPTION MASS SPECTROMETRY

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Abstract

Temperature-programmed desorption mass spectrometry (TPD MS) is discussed with reference to studies of modified pyrogenic oxides. Simple theoretical models are presented in order to allow an approximate analytical treatment of TPD MS data. Rate constants for first- second- and third-order reactions have been obtained. Products of thermal decomposition of carbonized surface layer has been observed and identified. The different pathways of uni- and bimolecular desorption were investigated and rate constants of reactions has been derived from TPD MS measurements.

Adsorption and thermal stability of several polyketides has been studied by TPD MS in condensed and adsorbed states. Mass spectrometric analysis allowed observing correlation between chemical structure of morine and venorutone molecules and mechanism of thermolysis. Decomposition of carbon carcass of chromone, the bensanelled γ -pyrone in particular, resulted in formation of fragments with mass numbers 91, 95, 108, 111 m/z. Decomposition occurred in three stages with maxima at 200, 280, 380°C for morine and 240, 320, 450°C for venorutone. Presence of carbohydrate residue (ramnose, glucose) in venorutone molecule caused two additional stages of thermolysis in comparison with morine, maxima being located at 220 and 280°C. In this case, different to previous one, the substituted γ -pyrone has been produced being characterized by mass numbers 72, 97, 102, 126 m/z. Comparison of adsorption parameters for venorutone and carbohydrates has shown that carbohydrate residue played main role in adsorption of venorutone molecules on ultrafine silica surface. The ring C of venorutone molecule stayed free in adsorption process which attested the fact that hydroxyl group in position 4', responsible for biological activity of flavonoids, did not participate in adsorption. It allows the ring C preserve its antioxidant, membrane- and capillary-stabilizing activity in bound state.

Introduction

The article "Desorption mass spectrometry and its applications in surface chemistry" [1] has been published by A.A. Chuiko, V.A. Nazarenko and V.A. Pokrovskiy in the Bulletin of Academy of Sciences Ukraine twelve years ago. It is interesting to compare some statements and predictions of this review with actual progress in research development of mass spectrometry applications in surface chemistry.

"Surface chemistry is such a science in which traditional approaches has almost depleted their abilities. New results may be obtained only by involving new methods and experimental ideas. There is no doubt that desorption mass spectrometry is useful for solving problems of surface chemistry, but opposite is also correct: models and methods developed in surface chemistry will give rise to understanding of unsolved problems of desorption mass spectrometry.

Disperse systems, used in surface chemistry are interesting and practically important species, but also difficult for studies by traditional experimental methods of solid-state physics.

From our point of view, the main difficulty which appears in interpretation of mass spectrometry of thermal desorption originates not from lack of experimental data, but from inability to derive maximum information about mechanisms and kinetics of surface reactions. As a result, quantitative interpretation of thermal desorption spectrums is difficult and often equivocal". The most significant statement, which have lead us finally in touch with fundamental problems of thermal analysis and non-isothermal kinetics, is as follows: "Our experimental scheme is almost similar to thermoanalytical measurements which are wide spread in investigation of solid state reactions. This similarity is not occasional. It is based on the similarity of processes under investigation. In many cases solid state reactions occur at interfaces and thus belong to surface chemistry".

At the moment, all quoted considerations seem to be still adequate. Below in this article some attempts will be presented of overcoming theoretical and experimental problems mentioned in upper quoted text.

Almost in the same time when the article was published, the outstanding expert in solid-state reactions and thermal analysis, Professor David Dollimore from the University of Toledo, OH, USA, started thinking and working on thermal analysis of pharmaceutical compounds and other biomolecules. His first paper on thermal decomposition of aspirin was published in 1990, and series of his publications in this area [2-8] was completed by review article "Thermal Analysis" published in Analytical Chemistry [8] in 1996 in which section "Biological, Medical and Pharmaceutical Studies" was included.

Simultaneously we conducted research on surface chemistry of biologically active molecules in condensed state and adsorbed on ultrafine oxide surfaces by temperature-programmed desorption mass spectrometry method [9-20].

As a result, our scientific and personal contacts with D. Dollimore appeared at 1997. Mutual interest to the problems of non-isothermal kinetics in thermal analysis and TPD MS of biomolecules became a base of our fruitful cooperation in the framework of STCU project "Mass spectrometry of industrial aerosols in Ukraine" which was supported by him as Professor of Toledo University and as Honorary Member of Ukrainian Chemical Society.

Unfortunately, we have lost this outstanding scientist and fascinating person last year. Models and experimental data presented here were more than once discussed with David, so this paper is dedicated to his blessed memory.

Desorption models

For the interpretation of temperature dependencies of mass spectra we assume that the desorption equation may be expressed as

$$d\Theta / dt = -k\Theta^n \quad (1)$$

where Θ is the surface coverage varying in the interval $0 < \Theta < 1$, n the reaction order (assumed to be known from experimental data) and the desorption rate is

$$k = k_0 \exp(-E / KT) \quad (2)$$

where E_d is the activation energy of desorption and k_0 the pre-exponential factor (both parameters assumed to be known from experiments). At the initial condition $\Theta_{t=0} = 1$ we have the following solutions of equation (1):

$$\begin{aligned} \Theta(t) &= \exp[-\Phi(t)] & \text{for } n = 1 \\ \Theta(t) &= 1 / [1 + \Phi(t)] & \text{for } n = 2 \\ \Theta(t) &= 1 / [1 + 2\Phi(t)]^{1/2} & \text{for } n = 3 \end{aligned} \quad (3)$$

$$\text{where } \Phi(t) = \int_0^t k dt \quad (4)$$

In Fig 1 formulae (3) are illustrated for reaction orders $n=1,2,3$; linear law $T=T_0 + \beta t$ of temperature upon time dependence; and parameters of the model $\beta = 0.1 \text{ } ^\circ\text{K}\cdot\text{s}^{-1}$; $k_0 = 10^{13} \text{ s}^{-1}$; $E = 200 \text{ kJ}\cdot\text{mole}^{-1}$; $K = 8.31 \cdot 10^{-3} \text{ kJ}\cdot^\circ\text{K}^{-1}$. As Fig. 1 illustrates it, the less is reaction order, the steeper is the temperature dependence. More detailed information may be derived from the differential form of the dependence. In TPD MS experiment, due to uninterrupted pumping of desorbed compounds, the ion current of chosen component of mass spectrum is proportional to desorption rate of chosen product.

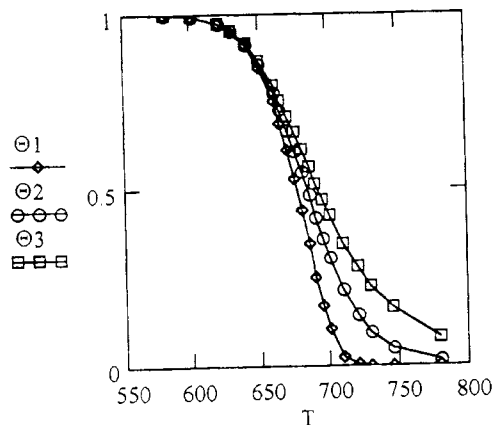


Fig. 1. Surface coverages Θ_1 , Θ_2 , Θ_3 as functions of temperature T for reaction orders $n=1,2,3$, correspondingly.

According to equations (3), the desorption rate which is directly proportional to the ion current can be obtained as

$$\begin{aligned} d\Theta(t)/dt &= -k \exp[-\Phi(t)] & \text{for } n=1 \\ d\Theta(t)/dt &= -k[1/[1+\Phi(t)]^2] & \text{for } n=2 \\ d\Theta(t)/dt &= -k[1/[1+2\Phi(t)]^{3/2}] & \text{for } n=3 \end{aligned} \quad (5)$$

Formulae (5) are illustrated by Fig. 2 in which desorption rates (proportional to derivatives of surface coverage) are presented as a function of the same parameters as were used in calculations of Fig. 1.

Equations (5) illustrate the typical temperature dependencies of the ion current, the second-order desorption curve being nearly symmetrical, the first-order curve decreasing faster on the high-temperature side and the converse being true for the third-order process.

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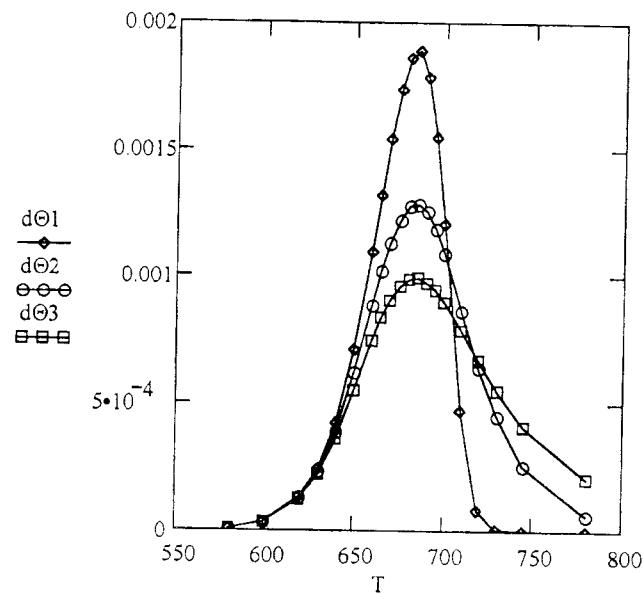


Fig. 2. Desorption rates $d\Theta_1$, $d\Theta_2$, $d\Theta_3$ as functions of temperature T for reaction orders $n=1,2,3$, correspondingly.

Taking into account the direct proportionality of $d\Theta / dt$ to the ion current, a simple procedure of treating the experimental data $I(t)$ may be proposed. The $\Theta(t)$ dependence on $I(t)$ may be written as

$$\Theta(t) = \Psi(t) / S, \text{ or } d\Theta / dt = -I / S, \text{ where } \Psi(t) = \int_t^\infty I dt; S = \int_0^\infty I dt$$

Using equations (5) and (6) we obtain

$$\begin{aligned} \ln k &= \ln[\Psi(t) / I] & \text{for } n = 1 \\ \ln k &= \ln[\Psi^2(t) / IS] & \text{for } n = 2 \\ \ln k &= \ln[\Psi^3(t) / IS^2] & \text{for } n = 3 \end{aligned} \quad (6)$$

Deconvolution procedure proposed by eqns. (6) is illustrated by Fig. 3. Model dependence for third order reaction (see $d\Theta_3$, Fig. 2) was chosen as an example of experimental thermogram. Three curves of desorption rate logarithm are presented as a function upon inverse temperature $\tau = (KT)^{-1}$ corresponding to three reaction orders $n=1,2,3$. Desorption rate parameters are the same as were used in calculations of Fig. 1.

If all the assumptions are allowable and the reaction order is a properly chosen whole number, n , then the function $\ln k = f(1/T)$ expressed according to equations (6) is linear over the full temperature range (in our case, $\ln k_3$ in Fig. 3). The advantage of the procedure involving equations (6) is the utilization of all data obtained experimentally, including those in the high-temperature part of the thermogram which is most important in estimating the adequacy of the model and, in particular, the reaction order, n . Besides, as it can be seen from Fig. 3, some additional simplifications are useful when operating with large amounts of TPD MS data. The key equation (4) may be expressed in

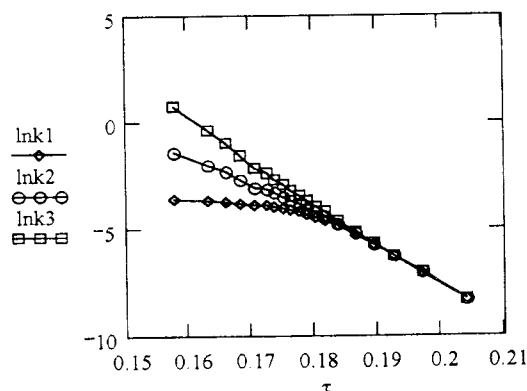


Fig. 3. Logarithm of desorption rate k for three values of reaction order as a function of inverse temperature $\tau = (KT)^{-1}$ calculated from eqns (6).

an approximate analytical form for a slow temperature ramp ($\beta < 0.1$ °K/s), high values of the pre-exponential factor ($k > 10^9 \text{ s}^{-1}$) and high maximum temperatures ($T > 450$ °K) as usually observed in experiments with chemisorbed organic molecules on a dispersed oxide surface.

Assuming a linear law, $T = T_0 + \beta t$ and expanding the temperature dependence near the maximum T_m , we obtain an approximate equation

$$\Phi(t) = \frac{KT_m^2}{E\beta} k_0 \exp\left(-\frac{E}{KT}\right) \quad (7)$$

which, in most cases, is valid within experimental accuracy. According to equations (5), the condition of maximum value of $d\Theta/dt$ (or ion current $I(t)$), is

$$\Phi(t) = 1 \quad (8)$$

$d\Theta/dt$ values calculated according to equation (7) for the first-order reaction with parameters $\beta = 0.1$, $T = 450 \text{ K}$, $k_0 = 10^9 \text{ s}^{-1}$ provide deviations from exact solution not exceeding 0.04 throughout the whole temperature range. This is the upper limit of possible inaccuracy of equation (7) in comparison with exact solution. The deviation of exact value T_m for a second-order reaction from this derived from equations (5), (7) is of order $2(kT_m/E)^2$, which is less than 2 K for upper values of pertinent parameters.

If the special features of the structure of the adsorption complex make necessary the introduction of the distribution function for surface sites, $N(E)$, then the total desorption rate $(d\Theta/dt)_s$ (and the total ion current, I_s) must be calculated as an integral

$$(d\Theta/dt)_s = \int_0^\infty \frac{d\Phi(t)}{dt} N(E) dE$$

Practically important chemically modified dispersed ultrafine oxides as models of industrial dust microparticles demonstrate interesting and unexpected effects both in thermal desorption and in decomposition of surface complexes, including phase transitions in adsorption layer. The application of various known multi-parameter models to systems of this kind carries the implicit danger that they only provide an adjustment to

the experimental data and foster the illusion of understanding, irrespective to adequacy of the of the model. So, the possibilities of any mathematical model, presented here in particular, are not to be overestimated. As was already emphasized in our previous work [15] an independent verification of the parameters obtained is always necessary which is not an easy task in the case of chemically modified dispersed systems. The advantage of our simple approach is that results are obtained in analytical form, which facilitates the computer treatment of experimental thermograms.

Temperature-programmed desorption mass spectrometry of carbonized silica

Oxide microparticles carbonized by the products of combustion are the main dust pollutant of the atmosphere in industrial areas using coal as a fuel. Though the effect of dust microparticles of such a kind on the human organism has not been studied in detail, it is clear that chemical reactions of biologically neutral compounds on the surface of carbonized oxide particles may result in their catalytic transformations into toxic compounds. Those compounds may be delivered to the human organism with the respirable fraction of aerosols or through drinking water. It is known that adsorption of drugs on enterosorbents cause their prolonged action; in the same vein, adsorption of the toxic compounds on the surface of dust microparticles may lead to prolonged exposure of toxins. Anyway, presence of incomplete combustion products known as strong toxins, carcinogens and mutagens on the surface of disperse oxides may result in serious hazard to human health.

Carbonization appears as complex, multi-stage process resulting in formation and growth of cluster-like germs of carbon phase. Under effect of temperature and duration of carbonization process the three-dimensional carbon lattice is formed, the number of hydrogen atoms decreases and the decrease of the number of sp^2 hybridized atoms in condensed polyaromatic systems is observed.

The surface layer may also include a large amount of chemisorbed molecules formed on the early stages of pyrolysis. Those surface complexes are the main source of polycyclic aromatic molecules, potential toxins, carcinogens and mutagens, which may appear as a result of catalytic reactions in the surface layer of carbonized disperse oxide. Heating of the carbon-mineral samples in vacuum is expected to destroy existing surface complexes and to release chemisorbed molecules. The composition of products and kinetics of thermal decomposition of surface layer of a carbon-mineral sorbent is a source of valuable information about mechanism of carbonization of oxide surface. The temperature-programmed desorption mass spectrometry is a reliable method of investigation the chemisorbed carbon-containing compounds. The method allows to find out not only the composition of chemisorbed molecules but also to estimate non-isothermal kinetic parameters of surface reactions, such as pre-exponential factors and activation energies.

The temperature-programmed mass spectrometry was used for analysis of volatile products of thermal decomposition of the carbon coated silica samples papers. The carbosil samples each of about 1 mg weight were placed in a quartz-molybdenum tube and evacuated at 10^{-1} Pa and then attached to the inlet system of a MI-1201 (Ukraine) mass spectrometer. The reactor-to-mass spectrometer interface included a high-vacuum valve with an orifice of diameter 5 mm and the inlet tube of 20 cm length, which was kept at 150 °C. The reaction space was open in the ion-source direction, and at the heating rate used (about $0.1^\circ\text{K}\cdot\text{s}^{-1}$) the observed intensity of the ion current was expected to be proportional to desorption rate so that diffusion inhibition might be neglected. We assumed quasi-stationary conditions when shape and position of desorption peaks did not depend on the temperature of the spectrometer interface, the sample dispersivity and/or its size. The TPD data were not considered further if these conditions were not fulfilled.

The desorption mass spectra were recorded in the 10 - 220 Dalton range and the temperature step was about 10 °K. Mass spectra of decomposition products are presented in Fig. 4 for four temperatures.

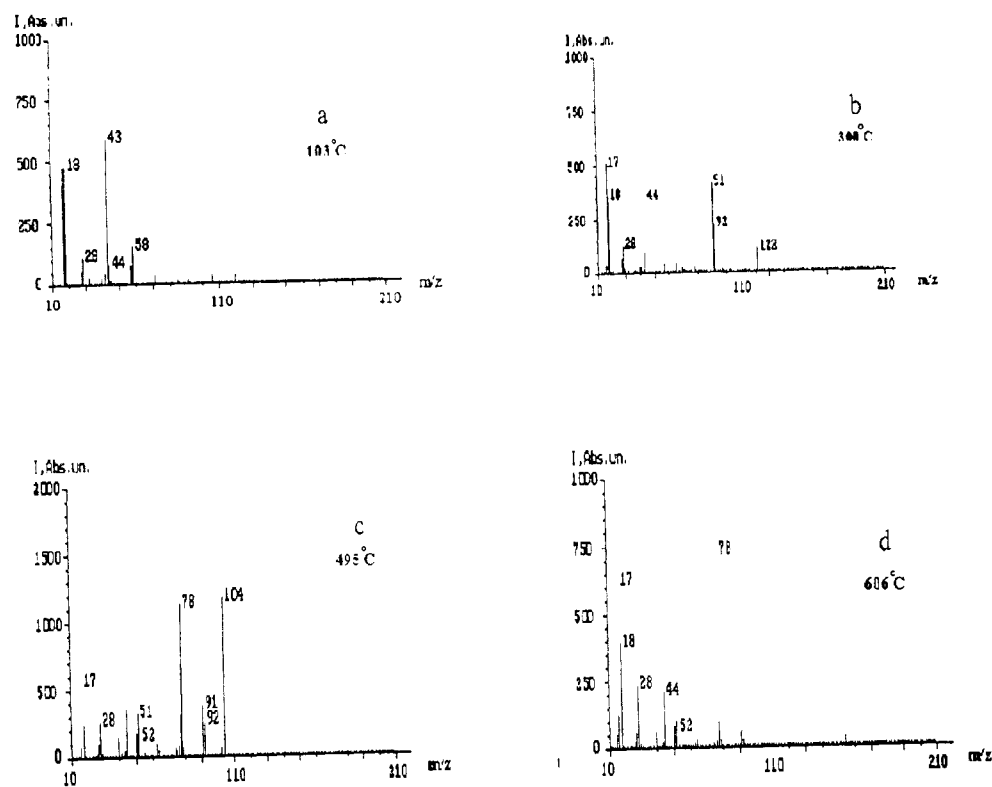


Fig. 4. TPD mass-spectra obtained upon decomposition reactions of phenylethanol bound to silica gel surface at: 103 (a), 300 (b), 495 (c), and 606 °C (d).

The first mass-spectrum (Fig. 4a) corresponding to 103 °C includes the m/z lines at 43 and 58 as the main components except water (m/z at 18 and 17). Their origin can be easily explained from the availability of adsorbed acetone used upon sample pretreatment. Its TPD maximum lies at ca. 100 °C. It should be noted that the lines corresponding to N,N-dimethylformamide used in parallel with acetone upon sample preparation were not observed in any spectrum.

The next mass-spectrum (Fig. 4b) obtained at 300 °C involves the m/z lines at 91, 92, and 122 caused by desorption of phenylethanol (this temperature corresponds to its maximal desorption). The main lines (m/z at 51, 78, 92, 91, and 104) in the spectrum obtained at 495 °C (Fig. 4c) attest that phenylethylene and toluene desorb. The formation of phenylethylene is due to unimolecular decomposition of bound phenylethanol with H transfer from the CH_2 group (nearest to aromatic ring) to O from $\equiv\text{SiOR}$ group. Analogous mechanism of decomposition of butanol bound to the silica surface was studied in our previous work. However, kinetics of such processes for bound phenylethanol and butanol essentially differed.

The last mass-spectrum (Fig. 4d) obtained at 606 °C includes the lines corresponding to benzene (m/z at 78) and biphenyl (m/z at 154). Inasmuch as the

existence of these molecules in the surface layer at such temperature is improbable, they can be formed due to migration of phenyl radicals along the surface and their interaction with $H^{\bullet}$ or bound H (benzene formation) or bound C_6H_5 or free $C_6H_5^{\bullet}$ (biphenyl formation). At the temperatures above 600 °C, the thermal transformations of bound organics have come to an end and only background lines are observed.

The temperature dependencies of the main components of the mass-spectra observed are shown in Fig. 5.

Phenylethanol desorption occurs in the 200 - 450 °C range and it is maximal at ca. 300 °C. For phenylethylene, the temperature interval width of desorption is the same but it shifts to higher temperatures (300 - 550 °C) with a maximum at 450 °C. The thermogram of phenylethylene (m/z at 104) desorption has asymmetrical shape, which is typical for first order reactions. The thermogram of m/z at 91 has two maxima at 300 and 470 °C that can be explained from the origin of the fragment $C_6H_5CH_2^+$ (responsible for m/z at 91) observed in the electron impact mass spectra for phenylethanol (m/z at 122), phenylethylene (m/z at 104), and toluene (m/z at 92); therewith, the first maximum of m/z at 91 corresponds to phenylethanol desorption. A benzene spectrum (m/z at 78) is observed in the 300 - 700 °C range and its shape indicates that $C_6H_6^+$ ion is formed through to two mechanisms.

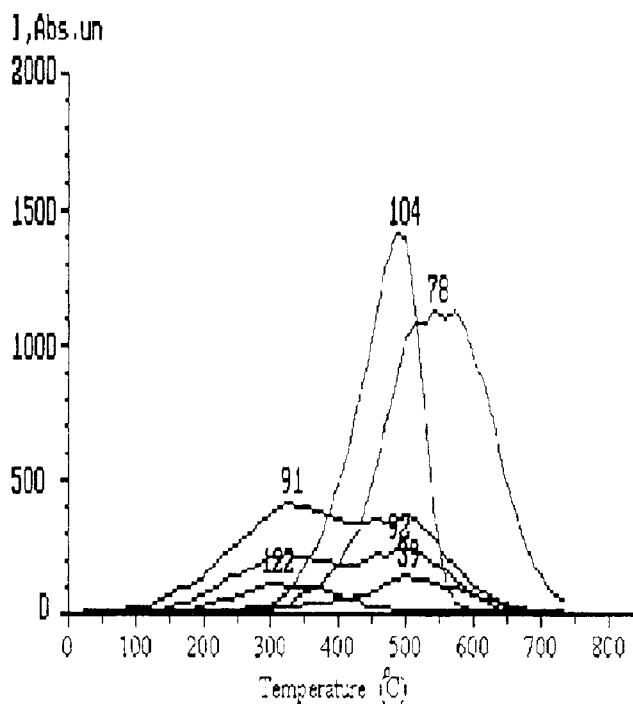


Fig. 5. Thermograms of desorption of phenylethanol (m/z at 122 and 91), phenylethylene (m/z at 104 and 91), toluene (m/z at 92, 91, and 39) and benzene (m/z at 78 and 39).

At low temperatures (300-500 °C), this ion is generated as a fragment of phenylethylene or phenylethanol and, at high temperatures (500-700 °C), it is obtained via ionization of benzene eliminated (see Fig. 5). The deconvolution of the benzene TPD spectrum according the origin of $C_6H_6^+$ shows that its width after subtraction of the contribution by the decomposition of desorbed phenylethylene is close to that for phenylethanol and phenylethylene (about 250 °C). Consequently, broadening of spectrums for those desorbed compounds is closely related, thereby implying that it is

caused by similar features of the decomposition of groups bound to the surface of partially carbonized silica. It should be noted that the maxima of desorption of benzene and biphenyl coincide. This fact points at common origin of both compounds due to recombination or capture reactions at the surface with the participation of mobile phenyl radicals. Biphenyl desorbs in more narrow high-temperature range than other products that give the higher values of k_0 and E .

Computation of kinetic parameters from this thermogram, according to the technique described in previous section, gives the values depending on a curve portions used for the calculations of a pre-exponential factor k_0 and activation energy E due to broadening of the spectra. The calculations of these parameters from the curve shape near the maximum give the k_0 and E values ($4.4 \cdot 10^5 \text{ s}^{-1}$ and 85 kJ/mole, respectively) close for obtained for the total curve. Underestimated value of the pre-exponential factor (caused by spectrum broadening) attests that the observed width of the spectrum is determined not only by the mechanism of the bound group decomposition but also by the dependence of the activation energy on the concentration of these groups and the surface heterogeneity.

Therefore, for the determination of the real k_0 and E values, additional information is needed. However, we can use an initial slope of the TPD spectra, where the influence of broadening factors is small, for the calculations of kinetic parameters. The values obtained for this part of the TPD curve for m/z at 104 and 103 are closely related and we can assume that they are close to the real values of kinetic parameters for desorption of phenylethylene.

Temperature-programmed desorption of polyketides from silica surface

Polyketides represent a wide class of natural biologically active compounds, which have similar biosynthetic origin. They play important role in living organisms participating, in particular, in oxidation-reduction processes. Typical representatives of polyketides are bioflavonoids, which are joined in the group of vitamin P. They are used in medical treatment of pathologic states caused by peroxide oxidation of membrane lipids. Immobilization of such compounds on the surface of ultrafine mineral matrices allows designing new medical forms with new useful properties. Studies on adsorption of polyketides and in particular on flavonoids on ultrafine oxide surfaces may, to some extent, clarify processes, which occur with those biomolecules on the cell membrane surface. The most interesting and promising is investigation of polyketide adsorption on high surface area silica because its isoelectric point is close to pH 2 whereas isoelectric point of majority of cells lies between pH 2 and pH 4. Thus, studies of adsorption on ultrafine silica surface may be useful in modeling such processes in living systems.

Our previous studies of vitamins and carbohydrates in condensed and adsorbed on the silica surface states by TPD MS method [10,13-14] has shown that this method is a promising tool in investigation of adsorption on high-surface-area oxides. The reason is that use of this method allow to compare thermal transformation of biologically active molecules in condensed state with that in adsorbed state and to find out peculiarities in thermal decomposition of molecules caused by adsorption.

Relatively high temperature used in temperature-programmed mass spectrometry makes possible for biomolecules to overcome activation barriers of such reactions which do not take place at low temperature, but can occur in living systems under effect of enzymes. Stable products of thermolysis identified in mass spectrometric experiment may be compared with biologically active molecules known in evolutionary allied or remote biological systems. For instance, it was found previously that oxygen free thermolysis of sugars (glucose, galactose, lactose, saccharose, raffinose) results in solid state biomimetic reaction with elimination of water molecule and formation in molecular form the substituted γ -pyrone, which is one of polyketides. It is known that biosynthesis of

polyketides is provided by acetyl-Kola which is formed in the process of sugar metabolism. Thus, some analogies are possible between chemical transformation of molecules and metabolism of molecules in living systems.

Experimental. Adsorption of venorutone half synthetic falconoid venorutone, the mixture of three isomers (3',4' and 7(β-oxy-ethyl)-3-ramnoglukoside-5-oxyflavon) on ultrafine oxide surface was done as follows. Adsorbent was preliminary treated at 400 °C for 2 hours in atmosphere. It was enough to remove the residue organic substances adsorbed on the surface. Aqueous solution of venorutone of 10 ml volume was mixed with 0.1 g of ultrafine silica (Aerosol A-300, specific surface area 300 m²/g) and kept at room temperature for two hours. Then suspensions treated in centrifuge, washed and dried at room temperature. Adsorption was studied in the concentration interval 10-350mg/l. Surface concentration was measured by spectrophotometer (wavelength λ=340 nm⁻¹) as concentration difference before and after adsorption. Mass spectrometry studies were conducted for venorutone surface concentration 2·10⁻³ g/g. Samples for mass spectrometric studies of quercetinum (3',4',3,5,7-pentaoxyflavon), morine, the structural isomer of quercetinum (2',4',3,5,7-pentaoxyflavon), 1,2-dioxiantra-quinone-3-sulfoacid (alizarine red S) in adsorbed state were obtained by their adsorption from water-alcohol mixture (50 %). Surface concentration on the silica surface for mentioned three compounds was about 10⁻⁸ mole/g.

Results and discussion. Adsorption and thermal stability of a row of polyketides: bioflavonoid quercetinum, half-synthetic flavonoid venorutone, alizarine red S - antraquinone and structural isomer of quercetinum - morine (see Fig. 6) has been studied. Those compounds were studied in condensed state and adsorbed on the surface of ultrafine silica by means of temperature-programmed desorption with mass spectrometry registration of decomposition products.

It was found that quercetinum and alizarine being heated in oxygen-free conditions are sublimed at the temperature of about 300 °C. During temperature-programmed experiment molecules of quercetinum and alizarine are condensed on the cool details of apparatus. No thermograms could be obtained for those compounds.

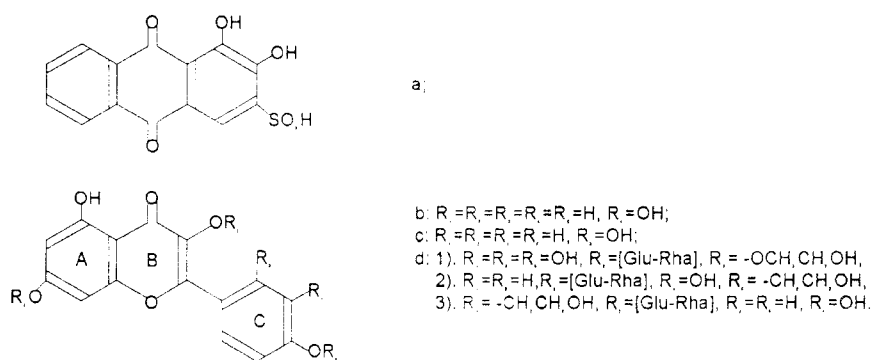


Fig. 6. Structures of polyketides: a: 1,2-dioxiantraquinone-3-sulfoacid; b: quercetinum; c: morine; d: venorutone (mixture of 1, 2, 3 isomers).

Molecule of morine is less stable in comparison with quercetinum and alizarine molecules. Bioflavonoids have the similar carbon carcass and characteristic location of oxide substituents which has its biosynthetic significance: ring A is usually hydroxillated over neighboring positions (5', 7') whereas in the ring C neighboring positions are hydroxillated (at first 4', then positions 3' and 5'). Morine, though having the same carbon carcass as quercetinum, has ring C hydroxillated in position 2' and 4' which is not characteristic for bioflavonoids. May be this is the fundamental difference of

bioflavonoids from morine - absence of intramolecular hydrogen bond in ring C. Alizarine is not a bioflavonoid but its molecule has two hydroxyl groups in ortho-positions which also can provide intramolecular hydrogen bond.

Mass spectrometric analysis allowed to find correlation between chemical structure of morine and venorutone molecules, on one side, and mechanisms of their thermolysis, on the other. In Fig. 7 the suggested scheme of morine decomposition is presented. Thermal decomposition of carbon carcass of chromone occurs by rupture of chemical bonds by mechanisms A, B, C.

In thermal decomposition mass spectra of morine (see Fig. 8) and venorutone the fragment of thermal decomposition of benzannelled γ -pyrone was observed which was characterized by following mass numbers: type A - 137, 136, 108, 91 m/z; type A - 141, 123, 112, 111, 96, 95 m/z; and also fragments of substituted aryl radical: type C - 109, 110, 111 m/z. It is to be noted that similar components of mass spectrum were observed in mass spectrum of quercetinum.

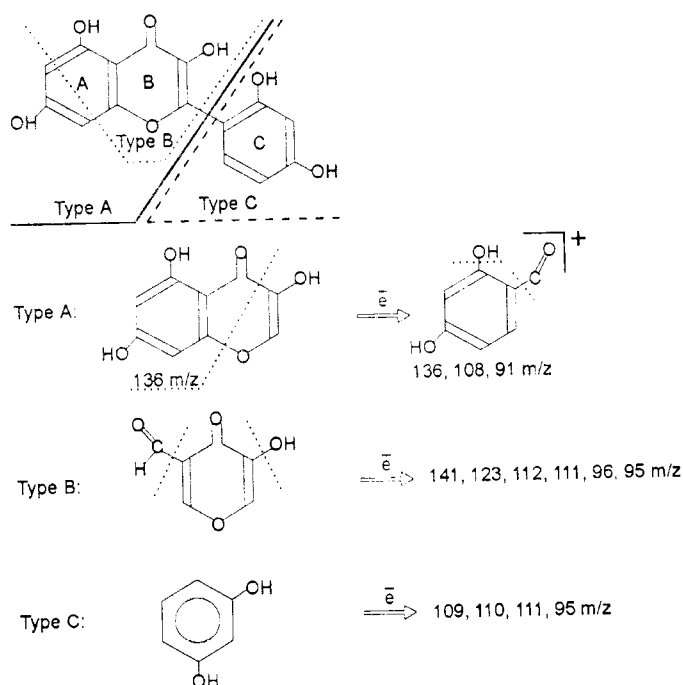


Fig. 7. Scheme of thermal destruction and fragmentation of morine molecule.

Thermolysis of 2-aryl-chromone occurs in three main stages (220, 280, 380 °C) for morine and in four stages (250, 360, 420, 480 °C) for venorutone (see Fig 9 and Table 1).

Analysis of mass spectrometric information shows that difference in structure of morine and venorutone molecules, in particular, different positions of hydroxillation of C-ring and presence of ethoxy-group in venorutone do not effect essentially the pathways of decomposition of benzannelled γ -pyrone. Presence of ethoxy-group explains intense lines at m/z 26, 28, and 43, in venorutone mass spectra. Presence of carbohydrate residue (ramnose, glucose) in venorutone molecule results in new specific features of thermal decomposition. In this case new stages of decomposition appear at the temperatures 250, 360 °C characterized by evolution of substituted γ -pyrone (72, 97, 102, 126 m/z). As it

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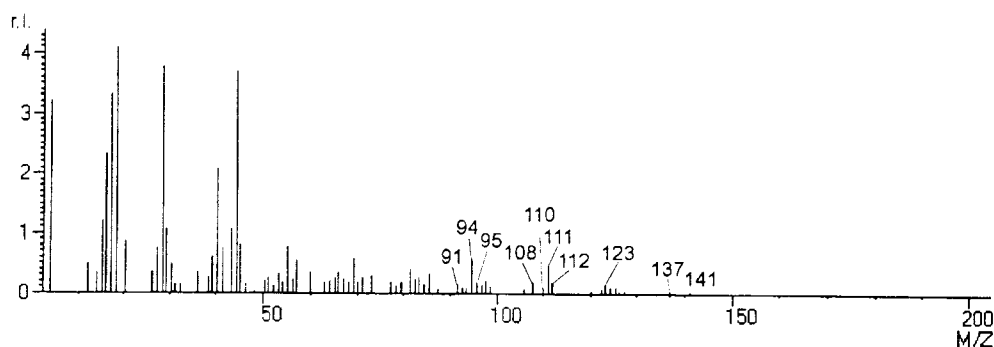


Fig. 8. Electron impact mass spectrum of morine thermolysis at 330 °C.

was found out in our previous work [19] thermolysis of carbohydrates including pyranose rings (glucose, galactose, lactose, saccharose, raffinose) results in formation this set of lines; thermolysis of disaccharides lactose and raffinose also occurs in two stages - 260 and 330 °C

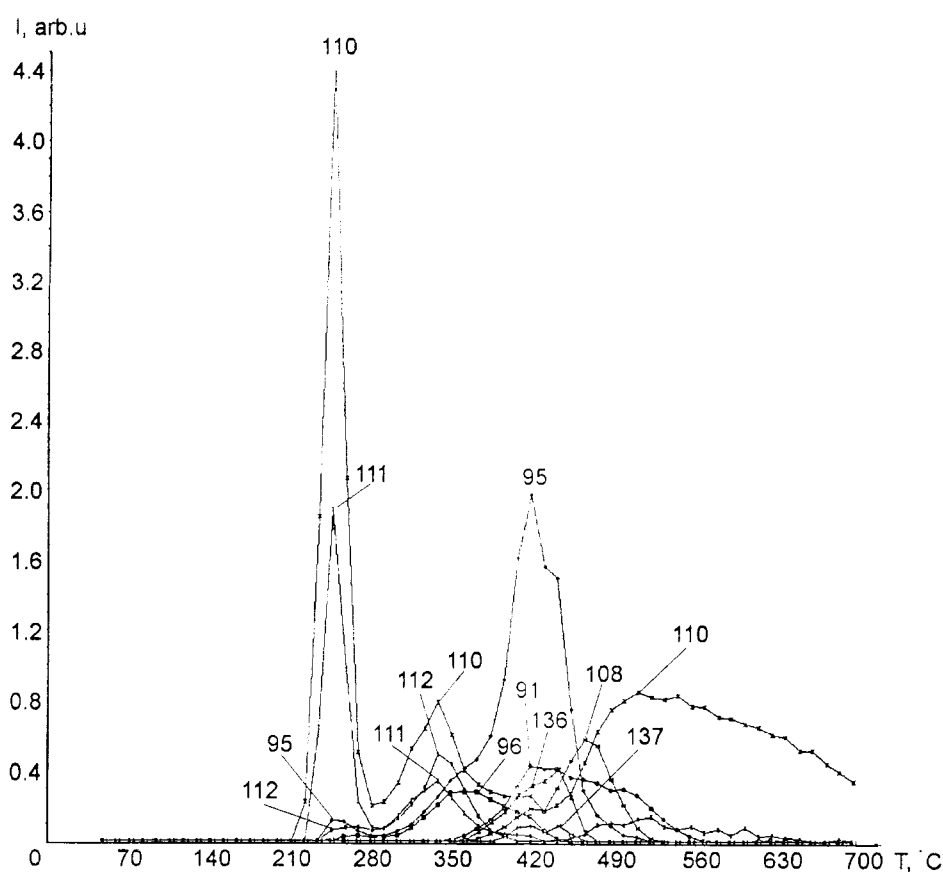


Fig.9. Thermograms of fragments m/z 137, 136, 112, 111, 110, 108, 96, 95, 91; thermal decomposition of 2-arylchromone - type A, D, C for venorutone in adsorbed state

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Table 1
Summarized data on decomposition of morine and venorutone

Num ber	T, °C	stage	Morine		Stag e	Venorutone condensed		Venorutone adsorbed	
			destruction type	m/z		destruction type	m/z	destruction type	m/z
1	180	-	-	-	-	-	-	I carbohydrate	126, 97, 72
2	220	2	chromone type A+B+C	136, 108, 91; 141, 123, 112, 95, 110	-	-	-	I chromone type C	109, 110, 111.
3	250	-	-	-	I	carbohydrate, chromone type B, C	126, 97, 72; 112, 95; 109, 110, 111.		
4	280	II	chromone type B	123, 112, 111, 95.	-	-	-	II carbohydrate, chromone type B, C	126, 97, 72; 112, 95; 110.
5	360	-	-	-	II	carbohydrate, chromone type B, C	126, 97, 72; 112, 111, 95.	III carbohydrate, chromone type B, C	126, 97, 72; 112, 95; 110.
6	380	III	chromone type A+B+C	108, 91; 123, 112, 95; 110	-	-	-	IV chromone type A	136, 108, 91
7	420	-	-	-	III	chromone type A	136, 108, 91	-	-
8	450	-	-	-	-	-	-	V chromone type A	108, 91
9	480	-	-	-	IV	chromone type A	136, 108, 91	-	-

Flavonoids in living organisms exist in the form of glycosides, on the last stages of biosynthesis in the form of methoxy- and methylen-dioxy- derivatives; that is why venorutone (mixture of 3', 4' and 7-(β -oxyethyl)rut sides, which is simultaneously glycoside and ethoxy-derivative of quercetinum, is most similar to physiologically active compounds among the investigated samples. Its adsorption from water solutions on the ultrafine silica surface has been studied. The adsorption isotherm has been obtained, the constant of adsorption equilibrium $E=2.013 \pm 0,106 \cdot 10^3$ l/mole, and adsorption change of Gibbs energy $\Delta G=18,8 \pm 1,2$ kJ/mole ($R^2=0,9882$). The value of adsorption limit for venorutone was $A_{\infty}=6,9$ μ mole/g and more than two order of magnitude larger than adsorption limit of alizarin red S and of quercetinum.

Venorutone in adsorbed state on the ultrafine silica surface was investigated by TPD MS. It was found out that main pathways of venorutone decomposition do not change after adsorption on the ultrafine silica surface. Nevertheless, additional maxima appear for 109, 110, 111 m/z in the vicinity of 220 °C (type C decomposition) and maximum for 126, 97, 72 m/z at 180 °C (decomposition of carbohydrate residue). Presence of those maxima being connected genetically with adsorption on the silica surface may be caused by the fact that carbohydrate residue takes part in adsorption mechanism. At higher temperatures number of decomposition stages, their location on temperature scale and sequence are similar to those in condensed state (See Table 1). Thus, as it is clear from Table 1 thermal decomposition of morine takes place in three main stages. Presence of carbohydrate substitution in chromone structure (venorutone) results in an additional stage of thermal decomposition; the decomposition of sugar residue and chromone type B and C takes place simultaneously. This may be explained taking into account that ramnoglucosil is located in the point 3 of chromone, i.e. participates in the structure which fragments we observe in thermolysis of B-type. Adsorption on silica surface demonstrate itself by appearance of maxima at high temperatures. The first stage (I) of thermolysis of carbohydrate residue the thermolysis of chromone of B-type is shifted to low temperature approximately to 40 °C in comparison with sugar, whereas during two next stages (II and III) thermolysis of chromone and carbohydrate residue occur simultaneously.

Practically important chemically modified dispersed ultrafine oxides demonstrate interesting and unexpected effects both in thermal desorption and in decomposition of surface complexes, including phase transitions in the adsorption layer. The application of various known multi-parameter models to systems of this kind carries the implicit danger that they only provide an adjustment to the experimental data and foster the illusion of understanding, regardless of the adequacy of the model. Therefore, the mechanistic implication of any mathematical model, and in particular of the one presented here, are not to be overestimated. An independent verification of the parameters obtained is always necessary but producing it is not an easy task in the case of chemically modified dispersed systems. The advantage of our simple approach is that the results are obtained in an analytical form, which facilitates the computer treatment of experimental thermograms.

Further accumulation of experimental data concerning TPD MS of dispersed oxides is necessary for a detailed understanding of the chemisorption mechanism, the structure of chemisorbed biologically active molecules and the non-isothermal kinetics of their decomposition.

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