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КИНЕТИЧЕСКИЕ ХАРАКТЕРИСТИКИ ГЕТЕРОГЕННОЙ РЕАКЦИИ ДИССОЦИАЦИИ МОЛЕКУЛ КОДЕИНА НА ОКИСЛЕННОЙ ПОВЕРХНОСТИ ВОЛЬФРАМА

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ВОЛЬФРАМДЫН КЫЧКЫЛДАНГАН БЕТИНДЕ КОДЕИН МОЛЕКУЛАЛАРЫНЫН ДИССОЦИАЦИЯСЫНЫН ГЕТЕРОГЕНДИК РЕАКЦИЯСЫНЫН КИНЕТИКАЛЫК МҮНӨЗДӨМӨЛӨРҮ

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KINETIC CHARACTERISTICS OF HETEROGENEOUS DISSOCIATION REACTION OF CODEINE MOLECULES ON OXIDIZED TUNGSTEN SURFACE

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Аннотация. Диссоциативная поверхностная ионизоация (ПИ) молекул кодеина исследовалась нестационарными методами ПИ в идентичных экспериментальных условиях на высоковакуумной масс-спектрометрической установке, оснащенной «черной камерой», охлаждаемой жидким азотом. Для предварительно адсорбированных молекул морфина были определены константы скорости диссоциации K_d и энергия активации E_d реакции разрыва связи, сопровождающейся образованием ионизируемых радикалов посредством поверхностной ионизации.

В процессе адсорбции молекул кодеина были получены константы скорости K_0, энергии активации термодесорбции E_0 и пред экспоненциальные множители в уравнении непрерывности для радикалов $C_9H_7N + CH_3$ $m/z = 144$.

Кроме того, была проведена термодесорбционная поверхностно-ионизационная спектроскопия молекул кодеина в атмосфере воздуха, и из спектров термодесорбции была определена энергия активации термодесорбции молекулы кодеина на воздухе.

Ключевые слова: нестационарная поверхностная ионизация, метод модуляции, метод модуляции напряжения, кодеин, адсорбция, радикалы, константы скорости и энергии активации термодесорбции.

Аннотация. Кодеин молекулаларынын диссоциациялык беттик иондошуусу (SI) стационардык эмес SI ыкмалары менен бирдей эксперименталдык шарттарда суюк азот менен муздатылган «кара камера» менен жабдылган жогорку вакуумдук масс-спектрометриялык түзүлүштө изилденген. Алдын ала адсорбцияланган морфин молекулалары үчүн диссоциацияланууылдамдыгынын константалары K_d жана беттик иондошуу аркылуу иондошуучу радикалдардын пайда болушу менен коштолгон байланыштын ажыратуу реакциясынын ак-

тивдешүү энергиясы E_d аныкталды. Кодеин молекулаларынын адсорбция процессинде ылдамдык константалары K_0, жылуулук десорбциянын активдештирүү энергиялары E_0 жана $C_9H_7N + CH_3$ $m/z = 144$ радикалдары үчүн үзгүлтүксүздүк тендемесинде экспоненциалдык факторлор алынды. Мындан тышкары аба атмосферасындагы кодеин молекулаларынын термикалык десорбциялык беттик иондоштуруу спектроскопиясы жүргүзүлүп, абадагы кодеин молекуласынын жылуулук десорбциясынын активдештирүү энергиясы жылуулук десорбциялык спектрлерден аныкталган.

Негизги сөздөр: стационардык эмес беттик иондошуу, модуляция ыкмасы, чыңалууну модуляциялоо ыкмасы, кодеин, адсорбция, радикалдар, ылдамдык константалары жана жылуулук десорбциясынын активдешүү энергиялары.

Abstract. The dissociative surface ionization (SI) of codeine molecules was investigated using nonstationary SI methods under identical experimental conditions with a high-vacuum mass spectrometric setup equipped with a liquid-nitrogen-cooled "black chamber."

For pre-adsorbed morphine molecules, the dissociation rate constants K_d and the activation energy E_d of the bond-breaking reaction accompanied by the formation of ionizable radicals through surface ionization were determined.

During the adsorption of codeine molecules, the rate constants K_0, the activation energies of thermodesorption E_0, and the pre-exponential factors in the continuity equation for $C_9H_7N + CH_3$ radicals with $m/z = 144$ were obtained.

Additionally, thermal desorption surface ionization spectroscopy of codeine molecules was performed in an air atmosphere, and the activation energy of thermal desorption of a codeine molecule in air was determined from the thermal desorption spectra.

Key words: nonstationary surface ionization, modulation method, voltage modulation method, codeine, adsorption, radicals, rate constants and activation energies of thermal desorption.

Introduction. The phenomenon of surface ionization (SI), particularly nonstationary SI processes, has found wide application in various fields of physics and chemistry, such as heterogeneous catalysis, nanotechnology, and materials science, where detailed information on the processes of particle–solid surface interactions is required [1–3].

When the equilibrium of an particle–surface system is disturbed by a change in experimental conditions (e.g., temperature or particle flux), the system relaxes to a new steady state over time. The relaxation kinetics can be described by monitoring the time-dependent current of ionized particles, which is proportional to the surface concentration $N(t)$ of adsorbed species. The time evolution of $N(t)$ satisfies the continuity equation:

$$\frac{dN(t)}{dt} = \nu - K(T)N(T) \qquad (1)$$

where ν represents the incoming molecular flux, T is the emitter temperature, and is the sum of rate constants of all heterogeneous processes that determine the loss of adsorbed species from the surface.

Although these relations have been studied extensively for atoms, much less information is available for polyatomic organic and bioorganic molecules. In such systems, the complexity of intramolecular bonding and multiple ionization pathways make quantitative analysis challenging. Particularly, nitrogen-containing organic molecules such as morphine, codeine, and related alkaloids exhibit rich dissociation behavior during adsorption and surface ionization processes, where radical and fragment formation may dominate over molecular desorption.

Previous works have addressed the stationary surface ionization (SSI) of codeine and similar alkaloids under equilibrium conditions [4-8]. Complementary studies employing various ionization methods—including electron ionization (EI), electrospray ionization (ESI), and chemical ionization (CI)—have been used to analyze their fragmentation and ionization pathways both in vacuum and atmospheric environments [9-18]. However, these techniques primarily describe static or equilibrium states and do not adequately capture transient surface reactions occurring under dynamically changing conditions.

Non-stationary surface ionization (NSSI) techniques, which involve the controlled modulation of either temperature, voltage, or molecular flux, make it possible to study such transient phenomena directly. By analyzing the relaxation behavior of the ion current in response to abrupt perturbations, one can derive kinetic parameters of both desorption and dissociative ionization. These methods have been successfully applied to simple adsorbates, but their use in analyzing the kinetics of complex organic molecules such as codeine remains limited.

In this context, the present study focuses on exploring the non-stationary surface ionization of codeine molecules adsorbed on oxidized tungsten. The combination of voltage modulation and flux modulation techniques enables precise evaluation of rate constants and activation energies associated with thermodesorption and heterogeneous dissociation reactions. The results provide deeper insight into the mechanisms of radical formation and molecular breakdown under dynamic surface conditions, offering a quantitative description of ionization processes for nitrogen-containing polyatomic systems.

Theoretical part. In surface ionization (SI), nonstationarity is induced by a sharp change in one of the parameters influencing the ion formation processes.

Depending on which parameter is varied, three main modulation approaches are employed: the flux modulation method (FMM), the temperature modulation method (TMM), and the voltage modulation method (VMM) [2]. We will consider the application of these methods as it was $N(t)$ n our work [22,23]. The time evolution of $N(t)$ satisfies the continuity equation:

$$\frac{dN(t)}{dt} = \nu - K(T)N(T) \qquad (1)$$

where ν is the flux of particles incident on the surface, and $K(T)$ represents the overall rate constant incorporating all elementary processes—such as adsorption, desorption, and dissociation—that contribute to the change in $N(t)$. Under non-stationary conditions, the total rate constant $K(T)$ is temperature-dependent and can be decomposed into several distinct contributions:

$$\frac{dN(t)}{dt} = \nu - K(T)N(T) \quad (2)$$

where K^+ and K^0 are the rate constants for ionic and neutral desorption, respectively, while K_d denotes the rate constant for heterogeneous dissociation of adsorbed molecules. For the individual processes, the temperature dependence of the rate constants follows Arrhenius-type relations:

$$K_M^+ = C_M \exp(-E_M^+/kT),$$
$$K_M^0 = D_M \exp(-E_M^0/kT),$$
$$K_{dM} = G_M \exp(-E_G/kT),$$

where C_M, D_M, and G_M are pre-exponential (entropy) coefficients, and E_M^+, E_M^0, and E_G correspond to activation energies of ionic desorption, neutral desorption, and dissociation, respectively.

During the heterogeneous dissociation reaction on the surface, i-th particles are formed. For the i-th dissociation product, the time-dependent surface concentration (n_i(t)) satisfies the following differential equation:

$$\frac{dn_i(t)}{dt} = v_i(t) - K_i(T)n_i(t), \qquad (3)$$

where $v_i(t)$ is the generation flux of the i -th species produced from the dissociation of the parent molecule, and $K_i(T)$ is the effective rate constant for its removal. The production flux $v_i(t)$ can be related to the dissociation rate as:

$$v_i(t) = K_{dMi}N(t).$$

By solving these equations, one can describe the temporal evolution of the adsorbed species and the corresponding ion current $I_i(t)$. For non-stationary conditions induced by voltage modulation (VMM), the ion current and the surface concentration follow an exponential relaxation law:

$$\Delta I \sim \Delta n_i = \Delta n_{max} \exp(-K_i(T)\cdot t) \quad (4)$$

where K_T represents the total effective rate constant. This indicates that as the system relaxes, the ion current decays exponentially,

reflecting the kinetics of desorption and dissociation processes.

In cases where the parent molecules have high ionization potentials and desorb primarily as neutral or weakly ionized fragments, the intensity of ionic desorption is mainly determined by the dissociation products. Thus, VMM is particularly useful for analyzing thermodesorption kinetics of radicals formed during heterogeneous dissociation of adsorbed molecules on oxidized tungsten surfaces [2, 22, 23]. For FMM, the system's response can be described by a sum of exponential functions:

$$n_i(t) = A\exp(-K_M t) + B\exp(-K_i t), \quad (5)$$

where A and B are constants determined by initial conditions, while K_M and K_i are the corresponding rate constants for the parent molecules and the resulting fragments. This relationship indicates that under both atomic and molecular ionization conditions, the buildup and decay of surface concentrations—and consequently, the ion currents—are nearly symmetric. Depending on whether $K_i \ll K_M$ or $K_i \gg K_M$, the current decay reflects either the average surface lifetime of the original molecule or the thermodesorption kinetics of its dissociation products [2,22,23].

The theoretical model presented here forms the basis for the quantitative analysis of non-stationary surface ionization processes of complex organic molecules, enabling the extraction of kinetic parameters from experimental modulation data.

A fairly straightforward way to determine the binding energy of particles adsorbed on a surface is to increase the temperature until desorption occurs. If the temperature is increased at a constant rate, the particles with the lowest desorption activation energy will be desorbed first, followed by particles with higher and higher desorption activation energies.

If we assume the presence of only one desorption activation energy and take a first-order expression for the desorption rate in the concentration of adsorbed particles, then the peak of the desorption rate will appear at temperature T_p, determined from the equation:

$$\frac{E}{RT_p} = \left(\frac{\nu}{\beta}\right)\exp\left(-\frac{E}{RT_p}\right) \quad (6)$$

where E is the activation energy, R is the gas constant, ν is the pre-exponential frequency factor, β is the heating rate. The frequency multiplier is usually taken equal to 10^{13} Hz and from here the desorption activation energy is determined.

The model developed by Falconer, Medix and King does not require taking into account the frequency multiplier. In this model, the temperature corresponding to the peak is related to the heating rate by the equation

$$Ln\left(\frac{\beta}{T_p^2}\right) = a - \frac{E}{RT_p} \quad (7)$$

where a - is a constant. By varying the heating rate so as to obtain peaks at different temperatures T_p the value of E can be determined T_p [24].

Experimental Part. A high-vacuum mass-spectrometric setup [21,22] was used for the studies. The preparation of the emitter (adsorbent) and the samples under investigation, as well as the experimental methodology, are described in our previous experiments [21,22].

To determine the kinetic characteristics in an air atmosphere, a surface ionization (SI) detector "Iskovich-1" [24] was used.

Results and Discussion. The kinetic parameters of radical thermodesorption for with were experimentally determined, along with the characteristics of the heterogeneous dissociation reaction of codeine molecules during their adsorption on the W_xO_y surface.

For these radicals, the activation energies of thermal desorption and sublimation were also determined [4].

The attraction of the nitrogen lone electron pair toward the emitter results in the development of a partial positive charge on the nitrogen atom. This, in turn, weakens the β-bonds ($C-H$ and $C-C$) adjacent to the nitrogen atom. The rupture of these bonds leads to the formation on the emitter surface of adsorbed radicals in the forms $[M-H]_{ads}$ and $(M-R)_{ads}$, possessing a low ionization potential (less than 6.5 eV). These radicals readily transfer an electron to the emitter and desorb as valence-saturated stable ions.

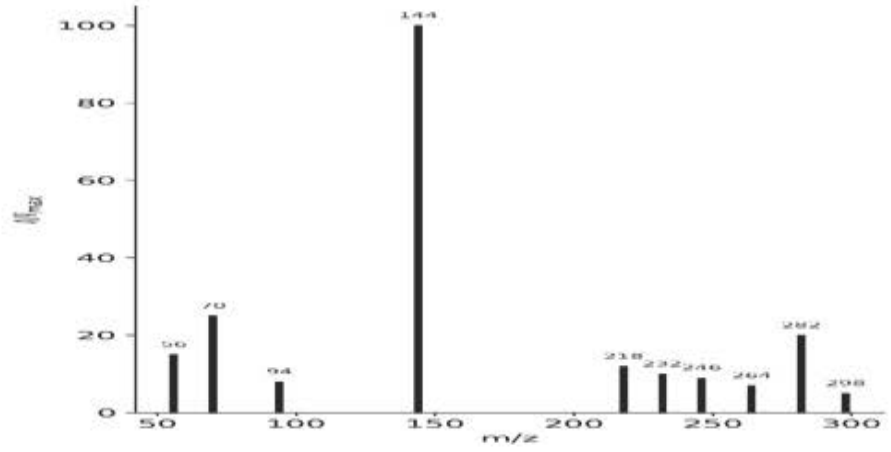

Fig.1. The mass spectrum obtained from the dissociative surface ionization (SI) of codeine molecules (T_e = 1000 K) [6].

The mass spectrum, as well as the temperature dependences of codeine molecules obtained during dissociative surface ionization, are presented in Figures 1–2.

It is primarily not the initially adsorbed molecules that desorb, but rather the products of the reactions occurring on the surface.

This behavior occurs because these radicals possess a relatively low ionization potential V, and they are ionized on the surface of oxidized tungsten with an ionization coefficient β that is close to unity.

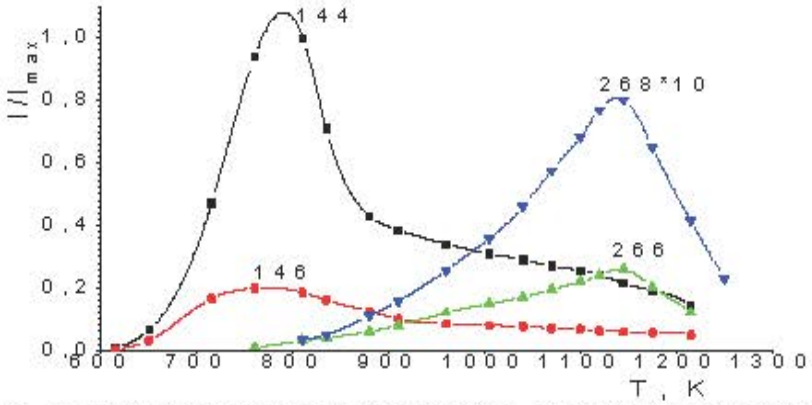

Fig.2. Dependences of the ion and radical currents during photoionization (PI) of codeine molecules. [6].

Figure 3 (a) and (b) show the dependencies of ln ΔI_i = f(t) obtained by non-stationary photoionization (PI) methods.

From these dependencies, the lifetimes of particles on the surface (Ki(t)) as well as the photoionization (PI) coefficient of the studied radicals were determined. It can be seen that the lifetimes obtained by FMM are 3-4 times longer than the lifetimes obtained by VMM.

Based on the experimental data obtained, the Arrhenius-type dependences

$$\mathrm{Lg}[K_i(T)\beta(T)] = \mathrm{Lg}K_i'(T) = f\left(\frac{1}{T}\right)$$

were constructed (see Figures 4 and 5). From these dependences, the activation energy E_i^+ and the pre-exponential factor C were determined.

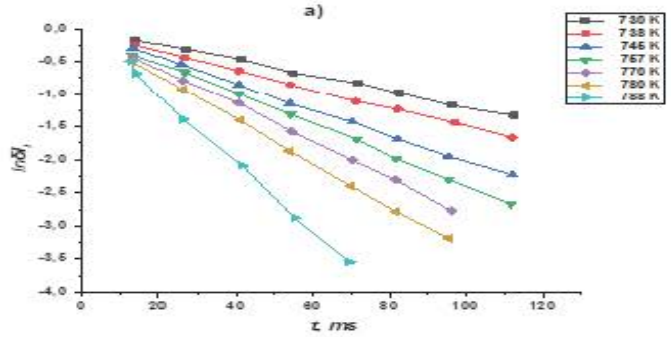

Fig.3. Dependencies $LnI_i(T) = f(t)$ in the dissociative photoionization of codeine molecules: (a) VMM and (b) FMM.

According to our considerations and previous studies, we attributed the results obtained in FMM to the kinetic characteristics of the heterogeneous dissociation reaction of codeine molecules on the surface [23]. In other words, the activation energy $E^{d,}$ of the heterogeneous dissociation reaction and the entropy factor G^* were determined.

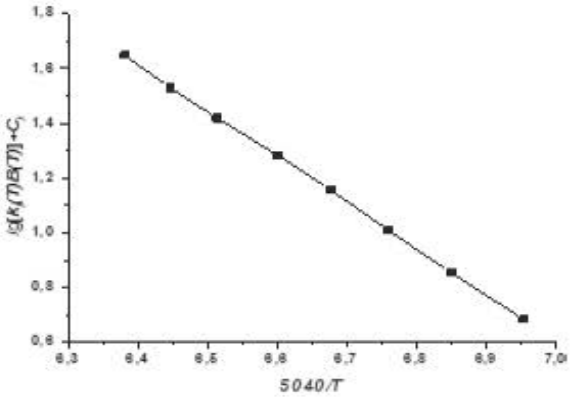

Fig.4. Dependence in ionization of codeine molecules for radicals $C_9H_7N^+CH_3$ (m/z144) under VMM conditions.

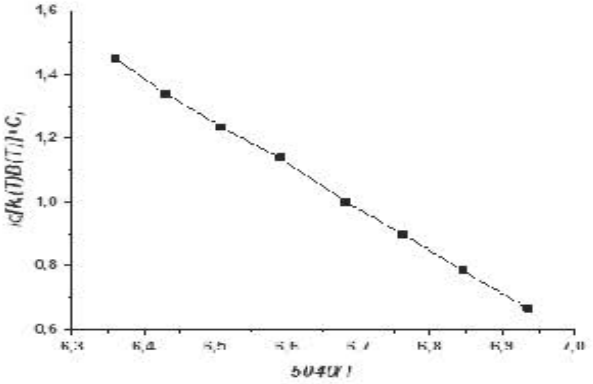

Fig.5. Dependence ionization of codeine molecules for the radicals $C_9H_7N^+CH_3$ (m/z144) under FMM conditions.

The obtained results for the radicals $C_9H_7N^+CH_3$ ($m/z = 144$) are presented as follows:

$$K^+_{144} = \frac{1}{\tau_{\text{ММН}}} = 10^{(12.5\pm1.0)} \cdot \exp\left[-\frac{1.7, \text{eV}}{kT}\right], \quad \lg C = 12.5;$$

$$K^0_{144} = \frac{1}{\tau_{\text{ММН}}} = 10^{(13.0\pm1.0)} \cdot \exp\left[-\frac{2.1, \text{eV}}{kT}\right], \quad \lg D^* = 13.0;$$

$$K^d_{144} = \frac{1}{\tau_{\text{ММІ}}} = 10^{(10.7\pm1.0)} \cdot \exp\left[-\frac{1.62, \text{eV}}{kT}\right], \quad \lg G = 10.7, \quad \beta = 0.82.$$

Figure 6 presents the thermal desorption surface ionization spectrum of codeine. It is evident that the spectrum exhibits a maximum temperature T_{max}, characteristic of each narcotic substance, which shifts toward higher temperature regions with an increasing quantity of substance applied to the evaporator.

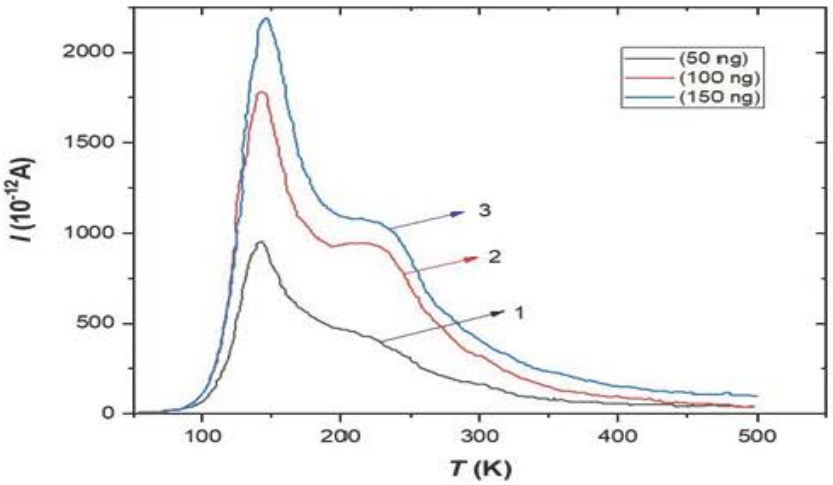

Fig. 6. Thermal desorption spectra of codeine CHS for different amounts of the substance: 1-50 ng, 2-100 ng, 3-150 ng.

Among various narcotic compounds, codeine displays the lowest maximum temperature. These temperature behaviors are typical for a specific geometry of the device and depend on the airflow rate through it, with an accuracy of approximately $\pm 5°$.

Using these dependencies and equation (7), we determined the thermal desorption energies under atmospheric conditions. The obtained result for the thermal desorption energy was E = 1.18 eV.

Conclusion. The adsorption, dissociation, and thermodesorption of polyatomic nitrogen-containing molecules such as codeine on oxidized tungsten have been systematically analyzed under non-stationary surface ionization conditions using both voltage and flux modulation methods. These complementary approaches enabled determination of key kinetic parameters, including the rate constants (K^+, K_0, K_d) and activation energies (E^+, E_0, E_d) associated with surface reactions. For the first time, the kinetic characteristics of thermodesorption and heterogeneous dissociation of the ($m/z = 144$) radical—formed during codeine adsorption—have been quantitatively determined. The data reveal that voltage modulation predominantly characterizes the kinetics of ionic desorption, while flux modulation provides more accurate information on molecular relaxation and surface lifetime. The obtained results demonstrate that the dissociative surface ionization of codeine molecules is governed by a sequence of bond

cleavage and radical formation processes that are strongly influenced by the oxide state of the tungsten surface. The activation energies and pre-exponential factors measured in this study contribute to a deeper understanding of molecular ionization mechanisms and adsorption–desorption dynamics of complex organic compounds under high-vacuum and controlled gas-phase conditions. These findings not only expand the existing knowledge on surface ionization kinetics but also have potential implications for analytical mass spectrometry, heterogeneous catalysis, and surface chemistry ionization kinetics but also have potential implications for analytical mass spectrometry, heterogeneous catalysis, and surface chemistry involving bioorganic molecules. involving bioorganic molecules.

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