

Determination of the kinetic characteristics of the heterogeneous reaction of dissociation of thebaine molecules on the surface of oxidized molybdenum

G. T. Rakhmanov^{a*}, B. E. Umirzakov^b, Z.R. Norboyev^a

^aNational University of Uzbekistan named after M. Ulugbek, Universitet street 4, 100174, Tashkent, Uzbekistan

^bTashkent State Technical University, Universitet street 5, 100095, Tashkent, Uzbekistan

*e-mail:rakhmanov.gt@mail.ru

Abstract

Dissociative surface ionization of $C_{19}H_{21}O_3N$ thebaine molecules with m/z 311 has been studied under unified conditions of nonstationary processes of surface ionization on the surface of oxidized molybdenum using unsteady methods of voltage modulation and flux modulation under unified experimental conditions. The rate constants K^d and the activation energy E^d of the dissociation reaction, the rate constants K^o and the activation energies of thermal desorption E^o , pre-exponential factors in the equation of continuity of pre-adsorbed thebaine molecules with bond rupture $(C - C_1)_\beta$ with the formation of ionizing radicals $C_{11}H_{12}ON^+$ (m/z 174) have been determined by means of surface ionization. The surface ionization coefficient β has also been determined, and the ionization potential of the studied radicals V has been estimated.

Keywords: surface, surface ionization, adsorption, desorption, sublimation, organic compounds, lifetime, rate constants of thermo desorption, activation energy, adsorption energy, non-stationary processes, flux modulation, voltage modulation, radicals.

Introduction

The development of areas of science and technology, such as nanotechnology and heterogeneous catalysis, microelectronics, and material sciences, and others, require detailed information about heterogeneous processes at the atomic and molecular levels. Non-stationary processes of surface ionization (SI) make it possible to determine the kinetic characteristics of thermal desorption (average lifetime of adsorbed particles with respect to their desorption in both charged and neutral states, activation energies of desorption and entropy factors in desorption equations), which allow a deeper understanding of the process of particle interaction with the surface of a solid body [1-3]. The dissociative SI of thebaine molecules on the surface of oxidized molybdenum will be studied by means of a non-stationary method of surface ionization—voltage modulation in the present research. The rate constants and activation energies of thermal desorption on the surface of oxidized molybdenum for these considered organic molecules have not yet been determined, although detectors for finding trace amounts of organic molecules of various classes mainly use thermal emitters made of oxidized molybdenum or iridium - molybdenum oxide. However, thebaine molecules have been well studied under stationary conditions by the SI method on the surface of oxidized tungsten [4–8]. In addition, thebaine has been studied by mass spectrometric methods, such as electron ionization (EI), electrospray ionization (ESI), chemical ionization (CI) and other ionization methods in vacuum and atmospheric air [10-19].

Non-stationarity is created by changing any parameter that affects the change in surface concentration $N(t)$ in case of SI. As is known, this change in concentration is determined by the concentration continuity equation [2]:

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

where v is the flow of particles arriving at the surface, T is the temperature of the adsorbent, $K(T)$ is the sum of the rate constants of all heterogeneous processes affecting the surface concentration of ionized particles. In the case of SI molecular flows $K(T)$ is defined as the sum of the rate constants of desorbing atoms in charged $K^+ = G \exp(-E_m^d)$, neutral states $K^0 = D \exp(-E^0/kT)$, where E^+ and E^0 are desorption activation energies, C and D are entropy factors, as well as the rate constant of the heterogeneous reaction of dissociation of molecules on the surface $K_m^d = G \exp(-E_m^d/kT)$, where E_m^d is the energy of the heterogeneous reaction of dissociation of molecules and G is the entropy factor.

The solution of this equation, as in the case of the voltage modulation method (VMM) [4] and the flux modulation method (FMM) [5], shows that the change in $n_i(t)$ and, accordingly, the ion current of i -particles $I_i(t)$ does not follow an exponential law and depend on both K_M and K_i . However, in the case of VMM, it is possible to distinguish cases when the change in current ΔI_i and the surface concentration of the i - particles Δn_i can be described by the following exponential dependence solution:

$$\Delta I \sim \Delta n_i = \Delta n_{\max} \exp(K_i(T) \cdot t) \quad (2)$$

There should be no increase in the surface concentration of the initial molecules $N(t)$ upon changing the polarity of the electric field of the VMM in order to do this. This is possible if $K_M^+ \ll K_M^0 + K_M^d$, for example, when the initial molecules are not desorbed in the form of ions due to the relatively high value of the ionization potential and their transformation on the surface into other particles ionized by SI. The products of dissociation of molecules in the form of ions are desorbed with high efficiency and M^+ is not desorbed [1]. Therefore, the kinetic characteristics of the thermal desorption of some polyatomic particles, including their radical products of the reaction of dissociation of the initial molecules on the surface of oxidized tungsten, were determined experimentally by VMM [6].

In contrast to VMM, FMM does not give unambiguous results for SI products of the reaction of dissociation of initial molecules. The solution to equation (3) for this case was obtained in [6]:

$$\Delta n_i = A \exp(-K_M(T)t) + B \exp(-K_i(T) \cdot t) \quad (3)$$

Thus, both in the case of ionization of atomic fluxes and in the case of dissociative SI of molecules under FMM conditions, the increase and decrease in the surface concentration and the ion current must be symmetrical, respectively. The difference lies in the fact that during the ionization of molecular flows, in the general case, the decline in the ion current is not an exponential function. However, if the dependencies $I_i(t) \sim n_i(t)$ obtained in the experiments turn out to be an exponential, then this means that one of the members included in them plays a dominant role in expressions (5). If $K_M \ll K_i$, then in this case $I_i(t) \sim n_i(t) \sim A \exp(-K_M(T)t)$ and the change in current over time of i -radicals determines the probabilities of loss and the average lifetime of the initial molecules from which they are formed on the surface of the emitter. If $K_m \gg K_i$, then $I_i(t) \sim n_i(t) \sim B \exp(-K_i(T)t)$ and in this case the current of the i - particles is determined by the kinetic characteristics of their thermal desorption. Further additional information is required in order to establish whether the quantities related to radicals or molecules are determined from the dependencies $\ln I_i(t) = f(t)$. This additional information is the study of such systems, the adsorbate-adsorbent under the same experimental conditions by the methods of VM and FM, since VMM always determines the kinetic characteristics of thermal desorption of the products of the heterogeneous dissociation reaction of the initial molecules. If the kinetic characteristics obtained by both methods coincide, that is, when $K_m \gg K_i$, the obtained characteristics can be attributed to the ionization of the products of the heterogeneous dissociation reaction of the initial molecules on the surface. If the results obtained by both methods do not coincide, then the values obtained by FMM can be attributed to the kinetic characteristics of the initial molecules ($K_m > K_i$). If molecular ions are not desorbed in the adsorbate-adsorbent system

of the molecule, but dissociate on the surface of the adsorbent with the formation of easily ionizable by SI radicals, then $K_M(T) \cong K_{Mi}^d(t)$ can be obtained from (3). Therefore, using VMM and FMM under the same experimental conditions, it is also possible to determine the kinetic characteristics of a heterogeneous dissociation reaction K_M^d the rate constant of a heterogeneous dissociation reaction, the activation energy E_M^d and the entropy factor G. The dissociative SI of thebaine molecules on the surface of oxidized molybdenum is studied in this research. The kinetic characteristics of thermal desorption and the characteristic times of the heterogeneous dissociation reaction on the surface for these considered organic molecules have not yet been determined.

Methods

A τ -spectrometer (high-vacuum mass-spectrometric setup) is used in the work. 10–12 μm thick, 50 mm long and 1 mm wide molybdenum tape is used as the emitter. After high-temperature annealing, the textured tape is oxidized in the mode described in [2-3] and has a work function $\varphi_n^* \cong 6.45 \text{ eV}$ and $\varphi_e^* \cong 6.2 \text{ eV}$. The emitter temperature is measured using a VIMP-015M pyrometer. The fluxes of the studied molecule are obtained by evaporation of substances from Knudsen cells made of quartz glass. The emitter is placed in a “black” chamber, all walls of which are cooled with liquid nitrogen. Therefore, only molecules “directly looking” from the hole of the Knudsen cell onto the central part of the emitter arrived at the emitter. The rest and scattering molecules are frozen on the wall of the “black” chamber. The residual pressure in the device is $\sim 10^{-6}$ Pa. The methodology of voltage modulation near the emitter surface is no more than 10^{-5} sec with an adjustable ion blocking time, with a delay signal establishment time as in [4–6]. In order to prevent “poisoning” of the emitter by the products of decomposition of the studied molecules [1]: the minimum fluxes of the studied molecules to the surface are used and the possibility of supplying an oxygen flow to the emitter surface ($\sim 5 \cdot 10^{13}$ mol/cm²sec) is provided.

Results and discussion

The kinetic characteristics of the thermal desorption of $\text{C}_{11}\text{H}_{12}\text{ON}^+$ radicals and the heterogeneous reaction of dissociation of molecules during the adsorption of thebaine molecules on the surface of M_xO_y is experimentally determined. The study of thebaine molecules is related to the fact that the SI of thebaine molecules are well studied under stationary conditions, as mentioned above [7, 9]: the sublimation energy [7], as well as the activation energy of thermal desorption in the air atmosphere [8], are determined. The structural formula of the $\text{C}_{11}\text{H}_{12}\text{ON}^+$ ion with m/z 174 is given in [7]. The mass spectra obtained during the ionization of thebaine molecules on the surface of oxidized molybdenum and the temperature dependences of the current of $\text{C}_{11}\text{H}_{12}\text{ON}^+$ radical ions coincide within errors with the dependences obtained in the work for the surface ionization of thebaine molecules on the surface of oxidized tungsten [7]. From the obtained mass spectra, it is seen that the products of the heterogeneous dissociation reaction are mainly desorbed, since they have a relatively low ionization potential V and these radicals are ionized on the surface of oxidized molybdenum with an ionization coefficient β close to unity. Therefore, for radical ions $\text{C}_{11}\text{H}_{12}\text{ON}^+ K_i^+ \gg K_i^0 + K_i^{d*}$, and in VMM we obtain a sharp peak of the ion current with an increase in the surface concentration n_i of ionizing particles. After having found out the transformation of the selected molecules, we carry out experiments to determine the kinetic characteristics of the thermal desorption of dissociative SI molecules of thebaine VMM and FMM under the same experimental conditions. $K_i(t)$ and the value of the SI coefficient of these radicals $\beta = \frac{\Delta I_i}{I_i}$ were determined from the dependencies on $\text{Ln } \Delta I_i = f(t)$ for different emitter temperatures. It is revealed that the lifetimes obtained in the FMM are 3-4 times longer than the lifetimes of the obtained VMM. Based on the data obtained, the Arrhenius dependences $\text{Lg}[K_i(T)\beta(T)]$ and $\text{Lg } K_i(T)(1 - \beta(T)) = f\left(\frac{1}{T}\right)$ are constructed, which are shown in Figures 1 and 2.

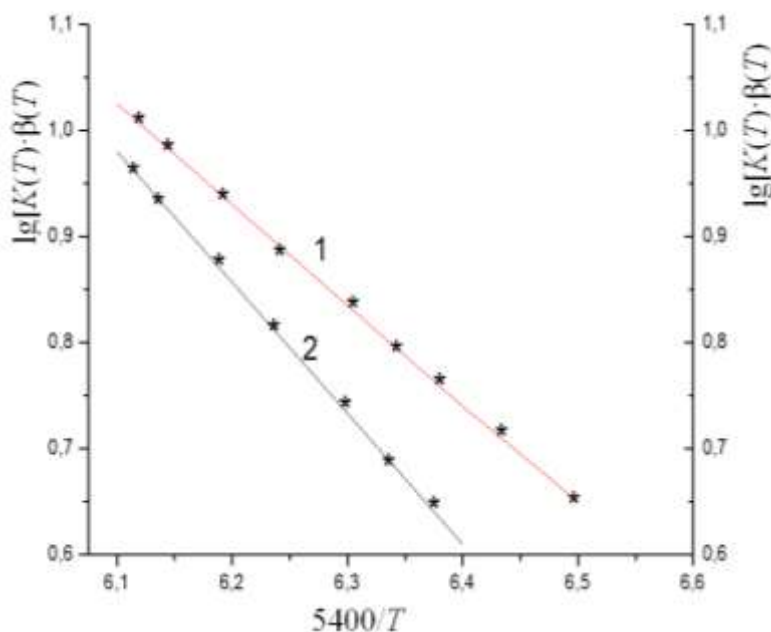


Figure 1. Dependence of $\lg[K(T) \cdot \beta(T)] = f\left(\frac{5040}{T}\right)$ on the ionization of thebaine molecules for radicals $C_{11}H_{12}ON^+$ ($m/z=174$): 1- in condition of VMM; 2- in condition of FMM.

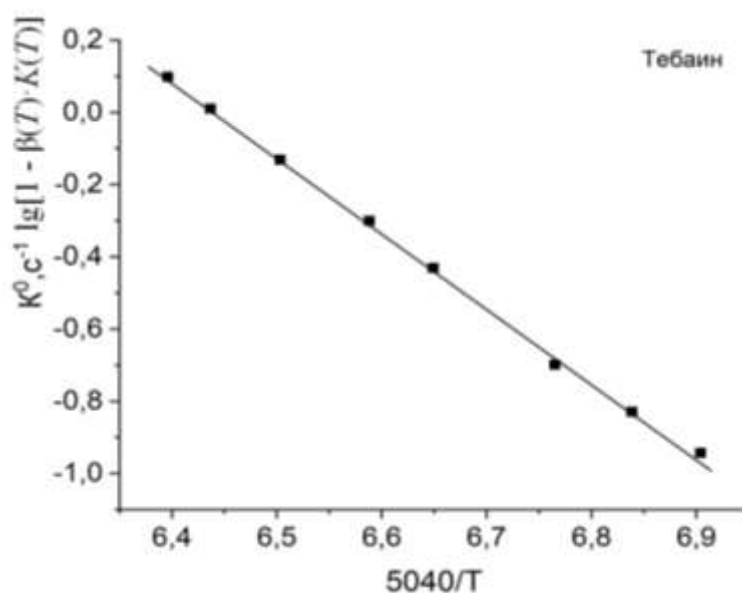


Figure 2. Dependence of $\lg[1 - \beta(T)] \cdot K(T) = f\left(\frac{5040}{T}\right)$ on the ionization of thebaine molecules for $C_{11}H_{12}ON^+$ ($m/z=174$) under VMM conditions;

The rate constants of thermal desorption in charged K^+ and in neutral states K^0 is determined based on these dependences. The results obtained by both methods do not coincide, and then the values obtained by FMM can be attributed to the kinetic characteristics of the initial molecules ($K_m > K_i$). If molecular ions are not desorbed in the adsorbate-adsorbent system of the molecule, but dissociate on the surface of the adsorbent with the formation of easily ionizable by SI radicals, then it can be obtained from (3) that $K_M(T) \cong K_{Mi}^d(t)$. Therefore, using VMM and FMM under the same experimental conditions, it is also possible to determine the kinetic characteristics of a heterogeneous dissociation reaction - K_M^d the rate constant of a heterogeneous dissociation

reaction, the activation energy E_M^d and the entropy factor G. The kinetic characteristics of thermal desorption and the characteristic times of the heterogeneous dissociation reaction on the surface have not yet been determined for these considered organic molecules. The obtained results of the study of the dissociative SI of thebaine molecules show that in our case it is possible to apply VMM and FMM, that is, there is a case when $K_M^+ \cong 0$, $K_M \cong K_M^d$, $K_i^+ \geq K_i^0$, $K_i^+ \geq K_i^0 + \sum_m K_{im}^d$. By reviewing [4-6] the results obtained in FMM (Figure 1) we attribute to the characteristics of the heterogeneous dissociation reaction of thebaine molecules, that is, we determine the activation energy of the heterogeneous dissociation reaction E^d and the entropy factor G. The results obtained are given in the following way:

$$K_{174}^+ = \frac{1}{\tau_{MMH}} = 10^{(12,1 \mp 1,0)} \exp \left[-\frac{1,80 eV}{kT} \right]; Lg C = 12,1$$

$$K_{174}^0 = \frac{1}{\tau_{MMH}} = 10^{(13,1 \pm 1,0)} \exp \left[-\frac{2,05 eV}{kT} \right]; Lg D = 13,1$$

$$K_{174}^d = \frac{1}{\tau_{MM\Pi}} = 10^{(10,1 \pm 1,0)} \exp \left[-\frac{1,64 eV}{kT} \right]; Lg G = 10,1$$
$$\beta = 0,64; \quad V \leq 6.6 eV$$

Conclusion

The study of the adsorption and dissociative SI of polyatomic molecules of nitrogenous bases on the surface of oxidized molybdenum using voltage modulation and flux modulation methods makes it possible to determine not only the rate constant K^+ and the activation energy of desorption in the form of E^+ ions of dissociation products of the initial molecule, but also makes it possible to determine the characteristic time of the heterogeneous dissociation reaction τ^d (or K^d) and the activation energy of the heterogeneous dissociation reaction of the initial molecules into ionizing particles. Also, the rate constant K^0 and the activation energy of thermal desorption E^0 of neutral particles are determined for the radicals $C_{11}H_{12}ON^+$ with $C_{11}H_{12}ON^+$ with m/z 174 during the adsorption of thebaine molecules for the first time.

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About authors

Umirzakov Baltakhodja Yermatovich, – doctor of physical-mathematic sciences, professor
Tashkent State Technical University, Universitet st. 5, 100095, Tashkent, Uzbekistan; Scopus
Author ID: 6603790401, ORCID: 0000-0003-2943-5844.

prof_sirojiddin@mail.ru.

Rakhmonov Ganiboy Tadjiyevich, – PhD of physical-mathematic science, associate
professor, National University of Uzbekistan named after M. Ulugbek, Universitet st. 4, 100174,
Tashkent, Uzbekistan;

e-mail:rakhmanov.gt@mail.ru

Norboev Zukhriddin Ravshanovich - Master student of the Faculty of Physics National
University of Uzbekistan named after. M. Ulugbek, st. University 4, 100174, Tashkent, Uzbekistan