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Study of dissociative surface ionization of thebaine molecules by non-stationary methods of surface ionization

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The adsorption and surface ionization of thebaine molecules ($C_{19}H_{21}O_3N$) c $m/z = 311$ on the surface of oxidized tungsten was studied by non-stationary methods of voltage modulation and flux modulation under the same experimental conditions using a high-vacuum mass spectrometric setup using a „black chamber“ all walls of which are cooled with liquid nitrogen. The rate constants K^d and the activation energy E^d of the reaction of dissociation of previously adsorbed thebaine molecules with bond cleavage $(C{-}C_1)_\beta$ with the formation of ionizable radicals by surface ionization have been determined. The rate constants K^0 and activation energies of thermal desorption E^0, as well as the pre-exponential factors in the continuity equation for $C_{11}H_{12}ON^+$ ($m/z = 174$) were determined during the adsorption of thebaine molecules C19H21O3N with $m/z = 311$.

Keywords: surface ionization, adsorption, non-stationary processes, thermal desorption rate constant, activation energy.

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Non-stationary processes of surface ionization (SI) provide an opportunity to determine the kinetic characteristics of thermal desorption (mean lifetime of adsorbed particles with respect to their desorption both in charged and neutral states, desorption activation energies, and entropic factors in desorption equations) and heterogeneous reactions of dissociation on a surface (heterogeneous dissociation reaction constants and characteristic reaction time) and thus gain a deeper understanding of the process of interaction of particles with a the surface of a solid [1–3].

In SI, non-stationarity is established by adjusting a certain parameter affecting the variation of surface concentration $N(t)$. This concentration variation is known to be governed by the concentration continuity equation [2]:

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

where v is the flux of particles to a surface, T is the adsorber temperature, and $K(T)$ is the sum of rate constants of all heterogeneous processes affecting the surface concentration of ionizable particles. In the case of SI of molecular fluxes, $K(T)$ is determined as the sum of rate constants of desorbing atoms in charged $K^+ = C\exp(-E^+/kT)$ and neutral $K^0 = D\exp(-E^0/kT)$ states (E^+ and E^0 are desorption activation energies; C and D are entropic factors) and the rate constant of a heterogeneous reaction of molecule dissociation on a surface $K^d = G\exp(-E^d/kT)$ (E^d is the energy of a heterogeneous reaction of molecule dissociation and G is the entropic factor).

Solving these equations using the voltage modulation method (VMM) [4] and flux modulation method (FMM) [5], one finds that the variation of surface concentration $n_i(t)$ of particles i (and the corresponding ion current $I_i(t)$) does not follow an exponential law and depends both on K_M and K_i. However, in the case of VMM, one may isolate certain instances where the variations of current ΔI_i and surface concentration $\Delta n_i(t)$ of particles i are characterized by the following exponential dependence:

$$\Delta I_i \sim \Delta n_i(t) = \Delta n_{\max}\exp\left[-K_i(T)t\right]. \tag{2}$$

A prerequisite for that is to avoid an increase in surface concentration $N(t)$ of the initial molecules on change of the VMM electric field polarity. This is possible if $K_M^+ \ll K_M^0 + K_M^d$ (e.g., in the case when the initial molecules do not desorb as ions due to a relatively high ionization potential and to their transformation on a surface into other particles ionized via SI). The products of dissociation of molecules desorb efficiently in the form of ions, while molecular ions M^+ of the studied sample do not desorb this way [1]. This is the reason why the kinetic characteristics of thermal desorption of certain polyatomic particles (including their radicals — products of dissociation of the initial molecules on the surface of oxidized tungsten) have been determined experimentally by VMM [6].

In contrast to VMM, the flux modulation method does not yield unequivocal results for SI of the products of dissociation of the initial molecules. The solution of Eq. (1) in this case was obtained in [6]:

$$\Delta n_i = A\exp\left[-K_M(T)t\right] + B\exp\left[-K_i(T)t\right]. \tag{3}$$

Thus, the rise and fall of the surface concentration (and, consequently, the ion current) should be symmetric

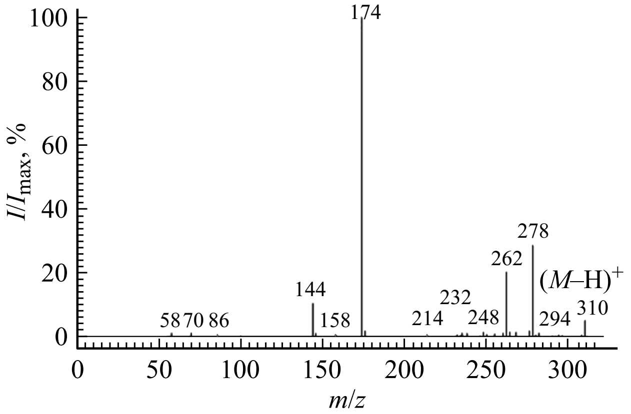

Figure 1. Mass spectrum of SI of thebaine on oxidized tungsten (emitter temperature $T_e = 1000\,\mathrm{K}$).

both in ionization of atomic fluxes and in dissociative SI of molecules under FMM. The difference is that, in the general case, the ion current fall in ionization of molecular fluxes is not exponential. However, if experimental $I_i(t) \sim n_i(t)$ dependences turn out to be exponential, it implies that one of the terms in expression (3) is dominant. If $K_M \ll K_i$, $I_i(t) \sim n_i(t) \sim A\exp[-K_M t]$, and the temporal variation of current of radicals i characterizes the loss probability and the mean lifetime of the initial molecules out of which they form on the emitter surface. If $K_m \gg K_i$, $I_i(t) \sim n_i(t) \sim B\exp[-K_i t]$; the current of particles i is then governed by the kinetic characteristics of their thermal desorption. Additional data are needed in order to determine whether the values derived from dependences $\ln I_i(t) = f(t)$ correspond to radicals or molecules. These additional data may be obtained by studying systems similar to adsorbate–adsorber ones using VMM and FMM under the same experimental conditions, since the kinetic characteristics of thermal desorption of products of a heterogeneous reaction of dissociation of the initial molecules is always determined in VMM. If the kinetic characteristics found with VMM and FMM match (i.e., $K_m \gg K_i$), they apply to the ionization of products of a heterogeneous reaction of dissociation of the initial molecules on a surface. In the contrary case, the values determined using FMM pertain to the kinetic characteristics of the initial molecules ($K_m > K_i$). If molecules in an adsorbate–adsorber system do not desorb as molecular ions but dissociate on the adsorber surface with the formation of radicals easily ionizable via SI, it follows from (3) that $K_M \cong K_M^d$. Therefore, applying VMM and FMM under the same experimental conditions, one may also determine the kinetic characteristics of a heterogeneous dissociation reaction: its rate constant K_M^d, activation energy E^d, and entropic factor G. The present study is focused on dissociative SI of thebaine molecules on the surface of oxidized tungsten. The kinetic characteristics of thermal desorption and the characteristic time of a heterogeneous dissociation reaction on a surface for these organic molecules have still remained undetermined. We report the results of examination of dissociative SI of thebaine molecules to which both VMM and FMM may be applied (i.e., the case with $K_M^+ \cong 0$, $K_M \cong K_M^d$, $K_i^+ \geqslant K_i^0$, $K_i^+ \geqslant K_i^0 + \Sigma_m K_{im}^d$, where K_{im}^d is the rate of dissociation of molecules into other (m) particle types, is feasible). Thebaine molecules have been studied thoroughly by using the SI under stationary conditions [7–9]. In addition, thebaine has been examined with the use of mass-spectrometric techniques, such as electron ionization, electrospray ionization, chemical ionization, and other ionization methods in vacuum and in atmospheric air [10–19].

A high-vacuum mass-spectrometric setup was used in the study. A tungsten strip with a thickness of $10\,\mu$m, a length of 40 mm, and a width of 1 mm served as the emitter (adsorber). Following high-temperature annealing, the textured strip was oxidized under the conditions specified in [2,3]. Its work function was $\varphi_i^* \cong 6.5\,\mathrm{eV}$ and $\varphi_e^* \cong 5.8\,\mathrm{eV}$. The emitter temperature was measured with a VIMP-015M pyrometer. Adsorbate fluxes were produced by evaporation of materials from Knudsen cells made from quartz glass. The emitter was introduced into a „black chamber" with all of its walls cooled with liquid nitrogen. Therefore, only the molecules with a „direct path" from the Knudsen cell aperture to the central emitter part reached the emitter. The other molecules and scattered molecules were frozen on the „black chamber" walls. The residual pressure in the device was $\sim 10^{-6}$ Pa. The method voltage modulation at the emitter surface was similar to the one used in [4–6] (with an adjustable ion suppression time and a signal delay time no longer than 10^{-5} s). In order to prevent contamination of the emitter with products of dissociation of the studied molecules [1], the fluxes of molecules to the surface were minimized; in addition, a hydrogen flow of $(\sim 5 \cdot 10^{13} \mathrm{mol}/(\mathrm{cm}^2 \cdot \mathrm{s}))$ could be supplied to the emitter surface.

The kinetic characteristics of thermal desorption of radicals $C_{11}H_{12}ON^+$ and the heterogeneous reaction of dissociation of molecules in adsorption of thebaine molecules on the W_xO_y surface were identified experimentally. Thebaine molecules were chosen for the fact that their SI was studied thoroughly under stationary conditions [7–9]: the sublimation energy [7] and the activation energy of thermal desorption in air atmosphere [8] were determined. The structural formula of a $C_{11}H_{12}ON^+$ ion with $m/z = 174$ was given in [7]. The mass spectra obtained in ionization of thebaine molecules on the surface of oxidized tungsten (Fig. 1) and the temperature dependences of the ion current of radicals $C_{11}H_{12}ON^+$ agree within the margin of error with those presented in [7]. It follows from the analysis of the measured mass spectra that products of the heterogeneous dissociation reaction are the ones most susceptible to desorption (since they have a relatively low ionization potential V), and these radicals are ionized on the surface of oxidized W with a near-unity ionization coefficient β. Therefore, $K_i^+ \gg K_i^0 + K_{im}^d$ for ions of radical $C_{11}H_{12}ON^+$, and a sharp peak of ion current is obtained

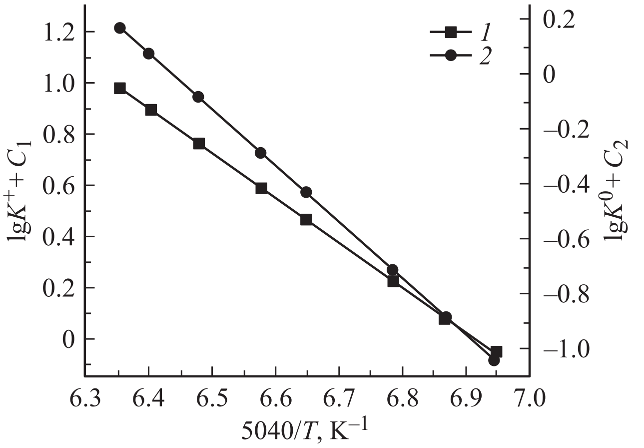

Figure 2. Dependence $\lg\left[K(T)\beta(T)\right] = f\left(\frac{5040}{T}\right)$ (*1*) and $\lg\left[K(T)\left(1-\beta(T)\right)\right] = f\left(\frac{5040}{T}\right)$ (*2*) in ionization of thebaine molecules for radicals $C_{11}H_{12}ON^+$ ($m/z = 174$) under VMM conditions.

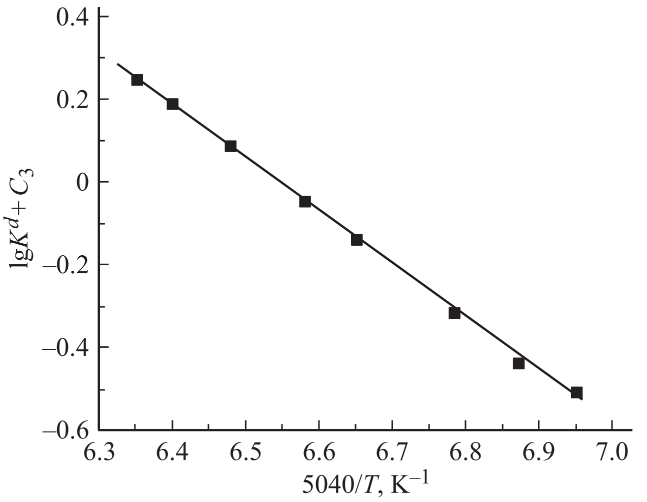

Figure 3. Dependence $\lg\left[K^d(T)\beta(T)\right] = f\left(\frac{5040}{T}\right)$ in ionization of thebaine molecules for radicals $C_{11}H_{12}ON^+$ ($m/z = 174$) under FMM conditions.

in VMM when surface concentration $n_i(t)$ of ionizable particles i increases. Once the specifics of transformations of the chosen molecules became clear, we performed experiments on determining the kinetic characteristics of thermal desorption of dissociative SI of thebaine molecules with the application of VMM and FMM under the same experimental conditions.

The values of K_i and SI coefficient $\beta = \Delta I_i / I_i$ of these radicals were determined based on dependences $\ln \Delta I_i = f(t)$ for different emitter temperatures. It was found that the lifetime obtained in FMM is 3−4 times longer than the one corresponding to VMM. These data were used to plot Arrhenius dependences $\lg\left[K_i(T)\beta(T)\right] = f(1/T)$ and $\lg\left[K_i(T)\left(1-\beta(T)\right)\right] = f(1/T)$ (see Fig. 2), which were then used to establish the rate constants of thermal desorption in charged K^+ and neutral K^0 states. Following [4–6], we identified the FMM results (Fig. 3) with the characteristics of the heterogeneous reaction of dissociation of thebaine molecules (i.e., determined activation energy E^d of the heterogeneous dissociation reaction and entropic factor G). The obtained results are presented in the table in the following form:

$$K^+_{174} = \frac{1}{\tau_{\text{VMM}}} = 10^{(12.1\pm1.0)} \exp\left[-\frac{1.75\,\text{eV}}{kT}\right], \quad \lg C = 12.1,$$

$$K^0_{174} = \frac{1}{\tau_{\text{VMM}}} = 10^{(13.2\pm1.0)} \exp\left[-\frac{2.05\,\text{eV}}{kT}\right], \quad \lg D = 13.2,$$

$$K^d = \frac{1}{\tau^d} = 10^{(10.1\pm1.0)} \exp\left[-\frac{1.54\,\text{eV}}{kT}\right],$$

$$\lg G = 10.1, \quad \beta = 0.72,$$

where τ_{VMM} is the lifetime determined by VMM.

The experimental error was ± 0.1 eV for the activation energy of thermal desorption and the heterogeneous dissociation reaction and ± 1 for $\lg C$, $\lg D$, and $\lg G$.

Thus, rate constant K^0 and activation energy E^0 of thermal desorption of neutral particles for radicals $C_{11}H_{12}ON^+$ with $m/z = 174$ in adsorption of thebaine molecules have been established for the first time. It has been demonstrated that the kinetic characteristics of thermal desorption of particles in the form of ions or neutral particles are always determined in VVM. Combining the obtained results with data on the sublimation activation energy and the energy of thermal desorption of organic compounds in air atmosphere, one may gain a deeper understanding of adsorption, desorption, and the processes of ion formation on a surface via SI in general.

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Conflict of interest

The authors declare that they have no conflict of interest.

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