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Studies of the Organic Molecules Dissociative Surface Ionization in the Mass-Spectrometric Surface Ionization Method

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Abstract : An improved voltage modulation method (VMM) was used to control the heat release and adsorption properties of the adsorbent. In this work, the voltage and flux modulation methods were considered under unified experimental conditions of dissociative surface ionization (SI) of polyatomic organic molecules, the criteria were found when under VMM conditions the current relaxation of SI carries information about the kinetic properties of thermal desorption of ionizable dissociation particles arriving on the surface of polyatomic molecules. Conditions were found under which the relaxation of the ionic current in the flux modulation method is determined by the kinetics of the heterogeneous dissociation reaction of the original polyatomic molecules. The values of the thermal desorption rate constant K^+ and the activation energy E^+ obtained with VMM for desorption of $(CH_3)_2NCH^+_2$ ions with *m/z* 58 by adsorption of imipramine and amitriptyline molecules agree well with each other and with the results for the desorption of the same ions by adsorption of other molecules. This confirms one of the basic conditions for the equilibrium process SI – the *a* degree (*β* coefficient) of the same particles SI on the same emitter surface is the same and does not depend on the way these particles are formed on the emitter surface.

Keywords : multi-atomic molecule, ionization, process, modulation, voltage, lifetime

Introduction

The development of physical electronics is characterized by a transition from adequately developed studies of the interaction of atomic particles with each other and with solid surfaces to studies of processes related to the interaction of complexes of atomic particles. These include, for example, studies of the adsorption of complex molecules, clustering, the interaction of accelerated molecular particles with a solid body, and the resulting nonlinear and nonadditive effects of cathode sputtering.

The determination of dissociative surface ionization of organic molecules, its revealed dependence on the physico-chemical properties of the molecule and the thermo-emission properties of the adsorbent provide information on the interaction of particles with the surface of a solid, which is fundamental not only for understanding the mechanism of ion formation, heterogeneous catalysis, but also for the operation of surface ionization (SI) devices.

SI of polyatomic particles has now been quite well studied,[1-6] the main regularities of adsorption processes, dissociation of initial molecules with the formation of ionizable products for various classes of organic compounds have been revealed, expressions for ionic currents have been obtained. Systematic studies on surface ionization of organic compounds of different classes were aimed at finding the classes of organic compounds capable of ionization on heated surfaces.[7] A review paper of Rasulev and coauthors[8] shows the results of the work on the development of SI methods and instruments for the detection and identification of nitrogenous bases.

Fujii's review[1] is devoted to the results of the author's development of SI/MS for organic compounds, and a review paper of Ishii et al.[2] lies on the application of SI/MS in forensic toxicology. In the paper of Ishii et al.[5] the SI of a series of molecules of complex compounds was studied: $(C_5H_5)_2Ni$, $(C_5H_5)Co$ on an emitter of oxidized rhenium. Other authors present the direction of methods for studying soil organic matter. And it was intensively investigated in direction of the technique of surface ionization mass spectrometry (SI/MS) and the method of selective step photoionization.[9-11]

A method for simultaneous determination of six commonly prescribed cyclic antidepressants and their major metabolites in urine is presented.[12] This method is useful for confirming drug abuse in medical professionals and in overdose cases where the identity of the abusing cyclic antidepressant is unknown. Hydrolysis has been shown to be important in the extraction procedure because tertiary cyclic antidepressants are highly conjugated in urine. Liquid chromatography with tandem mass spectrometry has been used to detect drugs in consumer saliva samples.[13] Morphine, codeine, and other drugs in the biofluid were quantified. The detection limit was a content of 2 ng/mL for each one sample. Melent'ev[14] has presented using of the gas chromatography mass-spectrometry (GC/MS) to determine opiates in human blood by multi-component analysis.

Kapustin and coauthors has demonstrated in their researches[15,16] that the efficiency and activation energy of selective ionization of some nitro compounds (TNT, HMX, RDX, etc.) were evaluated for the first time, and the process of selective ionization of a nitro compound (trinitrotoluene) on the surface of sodium vanadium oxide bronze under atmospheric conditions was studied.

Using reflectance difference spectroscopy to control the real-time coverage of phosphorus, the kinetics of tetrabutylphosphine adsorption and desorption of phosphorus from indium phosphide (0 0 1) were determined.[17] In the work on the determination of the kinetics of the dissociation reaction of polyatomic molecules, other methods were studied.[18–20] In this work, three methods used in the kinetics of radical reactions in liquid phase are described to estimate the dissociation energies of individual bonds in polyatomic molecules.[18] The first method is based on the study of equilibrium in radical dissociation reactions involving stable radicals and the measurement of the equilibrium constant. The second method is based on the study of the kinetics of homolytic decomposition of molecules. Measurement of the activation energy of such a reaction allows estimation of the dissociation energy of the weakest bond, such as the O–O bond in peroxides of different structure. The third method, developed within the framework of the intersecting parabolas model, is essentially to calculate the dissociation energy of the bond from the activation energy of the radical reaction involving the molecules in question. Using this method, we have been able to estimate the dissociation energies of C–H, N–H, O–H, and S–H bonds in a large number of organic compounds. The limitations and peculiarities of the application of each method are discussed, and the bond dissociation energies obtained with their help are given.

However, it is not always possible to unambiguously determine the characteristics of the individual stages of ion formation from the experimental dependencies, since the value of the ion current measured in the experiments depends at least on both the rate constant of the chemical reactions in the adsorbed layer and the rate constant of thermal desorption in the charged and neutral states of the reaction products formed in the adsorbed layer. On the basis of non-stationary SI processes of organic compounds, information on the kinetics of thermal desorption processes of multi-atomic particles is obtained.

Theoretical part

In organic compounds' molecules adsorption on solid heated surface, various heterogeneous reactions - chemical transformations of the initial molecules occur, depending on its catalytic activity. The products of dehydrogenation, association, and dissociation reactions, and in some cases the molecules themselves, can form ions during desorption. Therefore, the molecular current ν entering the surface of the emitter can be represented as a stream of i-efficient currents v_i, each of which forms only one type of particle. At the same time, there is a connection between ν and v_i (1):

$$v_i = v\gamma_i(T,E), \qquad (1)$$

where: $\gamma_i(T,E)$ is a coefficient that depends, for a given "molecule-emitter" pair, on the emitter temperature T and on the electric field strength E near the surface. It determines the concentration of the i-particle in the adsorbed layer as a result of all processes taking place in it.[21]

The coefficient depends not only on the characteristics of the dissociation processes of the initial molecules through a given channel leading to the formation of i-particles, but also on the rate constant of the subsequent dissociation and thermal desorption of these particles from the surface.[22] The ionization of each type of particle can be considered independent of the ionization of the other type in this representation. The SI degree of each type of particle is expressed by the formula (2):

$$\alpha_i = \frac{v_i^+}{v_i^o} = A_i \exp\left[\frac{e\left(\varphi + \sqrt{eE} - V_i\right)}{kT}\right] \qquad (2)$$

where: V_i - the first adiabatic ionization potential of the i-particle,

$A_i = \dfrac{Q_i^+}{Q_i^o}$ - the ratio of the total static sums of its

corresponding states, v_i^+ and v_i^o are particle fluxes in charged and neutral states, respectively; A – ratio of statistical weight states of positive ions and atoms at solid temperature T; e is the charge of the electron, φ is the work function of the electron leaving the solid; k – Boltzmann constant; E – external electric field strength; T – emitter temperature; V is the ionization potential of ionized atoms.

The general expression for the current of ions of each i-particle type in stationary ionization conditions (3):

$$I_i = e\nu_i S\beta_i = e\nu S\beta_i \gamma_i(T,E) = \frac{e\nu S\gamma_i(T,E)}{1 + A_i^{-1}\exp\left[\dfrac{e(V - \varphi - \sqrt{eE})}{kT}\right]} \quad (3)$$

Hence, in the case of difficult ionization (4):

$$I_i = e\nu S\gamma_i(T,E) A_i \exp\left[\frac{e(\varphi + \sqrt{eE} - V_i)}{kT}\right] \quad (4)$$

and in the case of light ionization (5):

$$I_i = e\nu S\gamma_i(T,E) \quad (5)$$

The dependence of $\gamma_i(T)$ has a strong influence on the dependence of $I_i(T)$. If $\beta_i(T)$ is unchanged, e.g., in the case of light ionization, formula (5) conveys the dependence of $\gamma_i(T)$, and the values of I_i are related as the values of $\gamma_i(T)$.

A peculiarity of the ionization of polyatomic organic compounds is that, as a rule, it is not the molecules themselves that are ionized, but the products of their chemical transformations in the adsorbed layer (Figure 1).

On the basis of studies of SI of more than five hundred nitrogenous compounds, the basic rules of ion formation have been established, which have predictive power. They allow the structure of the ions formed from the structure of the molecules. These rules can be easily explained with the help of the adsorption scheme of amines.

Adsorption of amines occurs by the formation of a coordination bond with the adsorbent: the pulling back of the disproportionate pair of electrons of the nitrogen atom toward the emitter, which occurs during this process, leads to the formation of a partial positive charge on the nitrogen atom (Figure 2a).[23]

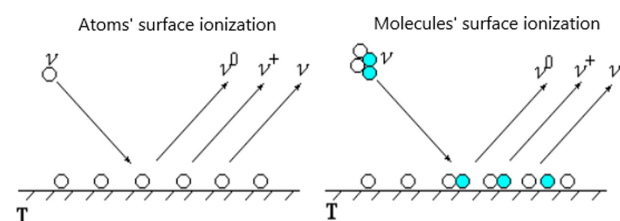This causes a significant weakening of the β-bonds with

Figure 1. The phenomenon of surface ionization (conventional symbols are used, since the dissociated radical consists of several different atoms, for example – $(CH_3)_2N = CH_2$.

respect to the nitrogen atom and leads to the possibility of formation of radicals (M-H) and (M-R) in the adsorbed layer, which are energetically advantageous for leaving an electron to the solid and are desorbed as ions with a 4-valent positively charged nitrogen atom with sp^2 hybrid orbitals (Figure 2b).

The measured lifetime τ of these radicals at the surface is relatively long;[22] in the time τ they come to thermal and charge equilibrium with the surface and, desorbed, are ionized by SI.

In the adsorbed layer, particles can form as products of the dehydrogenation reaction (M-H-2nH) and (M-Alk-2nH), where the largest number n corresponds to the dehydrogenation of alkyl radicals to form conjugated C=C multiple bonds.

As a result of the interaction of adsorbed molecules, $[M+H]^+$ ions can be formed. Therefore, $[M+H]^+$ ions are always observed at low temperatures of the thermal emitter when the concentration of adsorbed particles is increased.[24]

Non-stationary SI processes are used to determine the kinetic characteristics of desorbing particles (average lifetime of adsorbing particles with respect to their desorption in charged and neutral states, desorption activation energy, and pre-exponential multipliers in the desorption equation).[25]

In the case of SI products of chemical transformations of initial molecules on the surface. the change of the surface concentration of the *i-particles* n_i- (t) follows the following equation (6):

$$\frac{dn_i(t)}{dt} + K_i(T) \cdot n_i(t) = \nu_i(t) \quad (6)$$

where $K_i(T) = K_i^+ + K_i^0 + \sum_m K_{im}^d$, $\nu_i(T) = N(t)K_{Mi}^d$ effective flux of *i-particles* on the surface; $N(t)$ is a concentration of the initial molecules; K_{Mi}^d is the rate constant of the reaction of dissociation of the initial molecule to form the *i-particle*.

The solution to this equation is as follows (7):

$$n_i(t) = n_i e^{-K_i(T)t} + (N_1 - N_0)\frac{K_M^d}{K_i(T) - K(T)}(e^{-K(T)t} - e^{-K_i(T)t})$$
$$+ \frac{K_M^d N_i}{K_i(T)}(1 - e^{-K_i(T)t}) \quad (7)$$

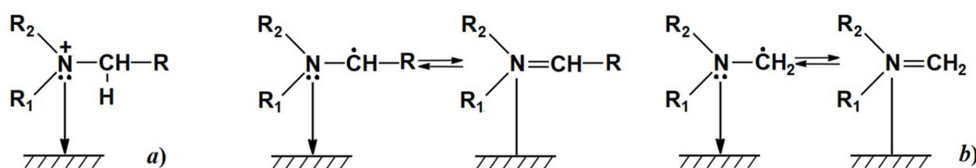The change in it with time I_i is determined as follows (8):

Figure 2. The mechanism of amines adsorption: a) - formation of a partial positive charge; b) - weakening of β-bonds and formation of radicals (M-H) and (M-R).

$$\Delta I_i = eC_i \exp\left(-\frac{E_i^+}{kT}\right) K_M^d \left[\frac{N_0}{K_i(T)+K_i^d(T)} - \frac{N_i}{K_i(T)}\right] e^{-K_i(T)t}$$
$$+ \frac{N_0-N_1}{K_i(T)-K(T)}\left(e^{-K(T)t} - e^{-K_i(T)t}\right) \qquad (8)$$

From the solution (4), it is clear that the change of current ΔI_i of the ions of *i-particles* does not follow the exponential law and depends on both K_M and K_i. However, in the voltage modulation method (VMM), we can distinguish cases where the change of current ΔI_i is described by the following exponent (9):

$$\Delta I_i \sim \Delta n_i = \Delta n_{max} \exp\left(-K_i(T)\cdot t\right) \qquad (9)$$

This assumes that the surface concentration of the parent molecules $N(t)$ does not increase when the polarity of the VMM electric field changes. This is possible, for example, in case of $K_M^+ << K_M^0 + K_M^d$, when the original molecules are not desorbed as ions due to the relatively high ionization potential and their transformation at the surface into other particles ionizable by SI. This is a common case in the practice of SI organic molecules when the dissociation products of molecules with high efficiency are desorbed as ions and M^+ is not desorbed.

In this case, the kinetic characteristics of thermal desorption of products of chemical transformations on the surface in the form of ions and neutral particles can be determined from the dependencies.

In addition, using the voltage modulation method, we can determine one of the most important characteristics of the SI - the surface ionization coefficient β (10):

$$\beta = \frac{i_{max}-i_0}{i_{max}} = \frac{\Delta i_{max}}{i_{max}} \qquad (10)$$

By determining the rate constant of thermal desorption $K(T)$ and the coefficient *SI* at each temperature using Arrhenius curves, the kinetic characteristics of thermal desorption of radicals, products of chemical transformations during adsorption, in the form of ions and neutral particles can be determined.

Experimental

A special mass spectrometric setup is required for the study SI of polyatomic particles by non-stationary methods. In addition to the study of SI in stationary mode, this setup will also allow studies of adsorption techniques and will contain the means to:

1) achievement of an ultra-high vacuum in the working chamber with the possibility to control the composition of the residual gas;

2) Mass spectrometric detection of ions desorbed from the surface;

3) Availability of a system that ensures both continuous delivery of the substances under study to the ionizing sur-

face and abrupt interruption of the particle flow;

4) The system's availability for sensitive registration and visualization of the ion current pulses of the desorbing ions;

5) Inclusion of methods to control and determine the thermo-emission characteristics of the ionizing surface, allowing control directly under the experimental conditions

6) Ensuring reliable determination of the temperature of the ionizing surface;

7) Availability of a commutation system that allows rapid switching of the system operation to different modes;

8) Use of a "black chamber" for freezing vapors of organic compounds in residual gasses.

To ensure these requirements, a special high-vacuum setup was constructed using the MX-7304 mass spectrometer (τ-spectrometer, "Electron", Sumy, Ukraine)). It includes both known technical requirements described in previous work and new ones. To reduce the vapor pressure of organic compounds under working conditions, liquid nitrogen was passed through the walls of the enclosure on which the ion source was mounted, creating a kind of "black chamber" (Figure 3).

Pumping was initially performed by the backing pump (2) and the vapor-oil pump TsVL-100 (3), which was connected to the pumped volume through a louvered water trap (5) and a metal-nitrogen trap (6) via a high-vacuum valve BB-(DU-40).

In order to improve the vacuum conditions and to pump oil-free under working conditions, an additional pumping line was introduced. In it a magnetic discharge pump NMD-0.16-1 was used (Prizma, Russian Federation). The pump was connected to the working chamber (1) through the high vacuum valve BB-2 (DU 631), which did not reduce the pumping speed of NMD-0.16-1 due to a large flow cross-section. Operating vacuum amounted to 1.0–3.0×10^{-6} Pa.

All nodes of the vacuum system were made of stainless steel without flanged joints with copper gaskets, which allowed the unit to heat up for a long time.
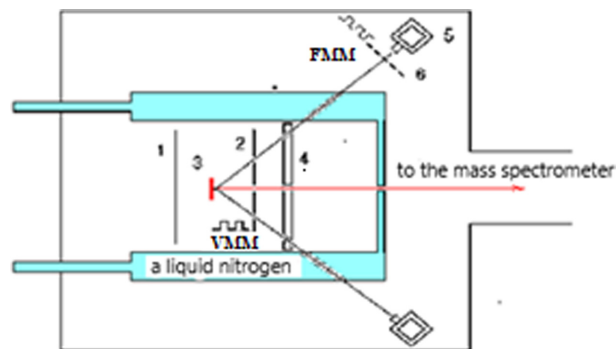

Figure 3. "Black chamber": 1 - modulating electrodes; 2 - focusing electrode; 3 - ion emitter; 4 - liquid nitrogen; 5 - Knudsen cell; 6 - overlapping platinum.

Heating of the whole unit to $T \approx 300\ ^oC$ was performed during operation of the vapor-oil pump with a trap filled with nitrogen for 4-5 h.

In the flow modulation method (FMM) mode, the modulation electrodes were used as focusing electrodes; in the VMM mode, they were used to modulate the ion current. The emitters of the source SI were $40 \times 1 \times 0.01$ mm textured tungsten ribbons. The emitters were stretched with tantalum springs. The length of the thermal emitters used was at least 40 mm with a width of 1 mm to ensure that the central part of the thermal emitter had a uniform temperature. Since it was necessary to use density-resistant molecular beams in the experiments, Knudsen evaporators were used as a source of molecular fluxes. They are quartz ampoules with a small hole d~0.8 mm in the center of the side wall. The ampoule was heated by passing a current through a tungsten coil wound directly on the ampoule. For uniform heating and thermal shielding, the ampoule was placed in a box-shaped housing made of tantalum.

The opening through which the test substance was loaded was sealed with a molybdenum plug. The molecular flow evaporator was adjusted so that the molecular flow of the test substance entered the working part of the thermal emitter through a system of membrane slits.

Oxidation of thermocouples was carried out in oxygen at a temperature of T 1100°K. Impurities of oxygen did not play a decisive role in tungsten emitters, so oxidation was carried out either with atmospheric oxygen or technical oxygen.

Amitriptyline and imipramine were purchased from Fortek distributor company (Sigma-Aldrich).

Results and Discussion

The resulting effect of solid surface processes is determined by the ratio of the values of the kinetic characteristics of adsorption, the heterogeneous process studied and thermal desorption. In this work the experimental determined the kinetic characteristics of thermal desorption of products of original molecules, radicals of $(CH_3)_2N = CH_2$ during adsorption of imipramine and amitriptyline molecules on the surface W_xO_y. The imipramine and amitriptyline molecules were chosen as the subject of studies on transient processes of organic compounds by the VMM because their SI have been well studied under stationary conditions.[26]

The adsorbates chosen were nitrogen-containing base molecules, which adsorb from organic compounds according to the established patterns of SI by using a disproportionate pair of electrons of the nitrogen atom to form a coordination bond with the surface. Withdrawal of the unshared nitrogen electron pair to the emitter results in the formation of a partial positive charge on the nitrogen atom. The latter causes weakening of the β-bonds (C-H and C-C) of the nitrogen atom in question. The breaking of these bonds leads to the formation of $(M-H)_{ads}$ and $(M-R)_{ads}$ radicals on the surface of the emitter, which have a low value of ionization potential (<6.5 eV) and easily give an electron to the emitter, which is desorbed as valence-saturated stable ions with a 4-valent positively charged nitrogen atom. The current density of such ions is, for example, up to ~5A/Torr·sm^2 in the adsorption of tertiary alkylamines and their derivatives on oxidized tungsten. Therefore, the selected substances (Table 1) should have been ionized with high efficiency to form ions of the dissociation products of the parent molecules (Figure 4).

The experiments showed that ion line $(M-R)_{\beta}^+$ is indeed the main line in the mass spectrum of imipramine's and amitripline's molecules (Figure 5, 6, and 7).

The mass spectrum of imipramine, due to the presence of the second heteroatom of nitrogen in the molecule, showed an intense line of $(M-R_i)_{\beta'}$ radical ions with m/z 58 Da in contrast to the main line of radical ions $(M-R_i)_{\beta}$ with m/z 208 Da, which was up to ~30% of the intensity of m/z 58 Da. In addition, in the mass spectra of all substances there
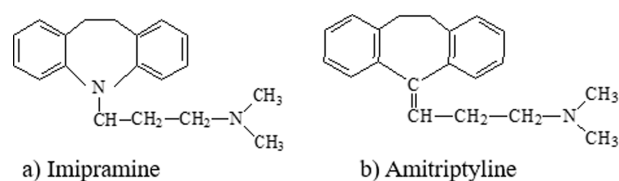
Figure 4. Imipramine (a) and amitriptyline (b) structural formulas.

Table 1. Kinetic characteristics of the interaction of polyatomic particles with the surface of oxidized tungsten.

Substance	Desorbing ions	Temperature range, K	E^+ eV	lgC	E^{0*} eV	lgD	β*
Imipramine $C_{19}H_{24}N_2$ (M = 280)	$CH_2=N^+{<}^{CH_3}_{CH_3}$	730-788	1.65	12.5	1.75	13.1	0.86
Amitriptyline $C_{20}H_{23}N$ (M = 277)	$CH_2=N^+{<}^{CH_3}_{CH_3}$	720-788	1.65	12.6	1.7	13.1	0.70

The bursts of currents of molecular ions are measured in relation to β, which are less than the true degree and coefficient of molecular SFI.
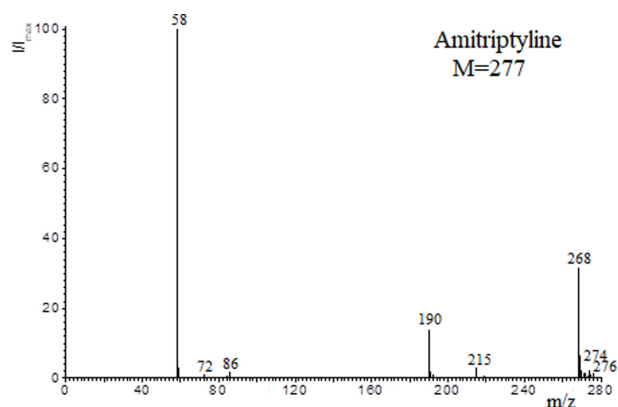
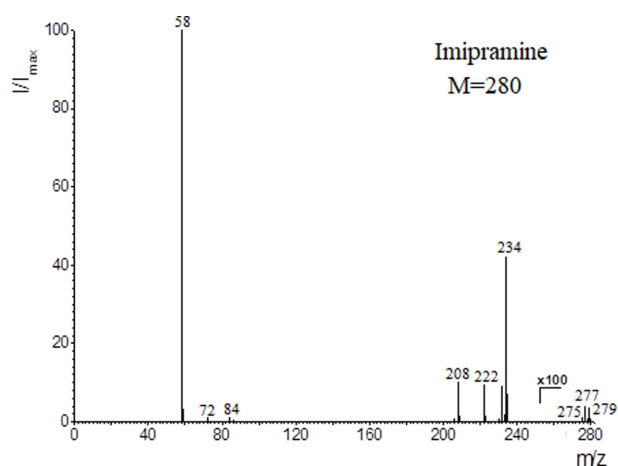**Figure 5.** Mass spectrum of surface ionization of imipramine on oxidized tungsten ($T_e = 100^\circ$K).

Figure 6. Mass spectrum of SI of amitriptyline on oxidized tungsten ($T_e = 100^\circ$K).

were lines of $(M-H)^+_\beta$ ions with an intensity of a few % of $(M-R)^+_\beta$. The mass spectra obtained by ionization of molecules on the surface of oxidized tungsten and the temperature dependence of the ion current of $(CH_3)_2N = CH_2$ radicals can be shown at Figures 5-7. The obtained mass spectra as well as the temperature dependence of the ionic current of ions with mass number m/z 58 are in good agreement with the results obtained earlier.[26]

Having found out the effective ionization of the products of chemical transformations of the selected molecule, the experiments to determine the kinetic characteristics of thermal desorption of dissociative surface ionization of molecules using the voltage modulation method was carried out.

At each emitter temperature, the maximum i_{max} and the minimum i_0, i.e., the stationary current, were determined from the oscillograms, and the ionization coefficients $\beta(T)$ were calculated from relation (10). Typical diagrams of ln $\Delta I_t = f(t)$ dependencies for various T-emitters are built. The
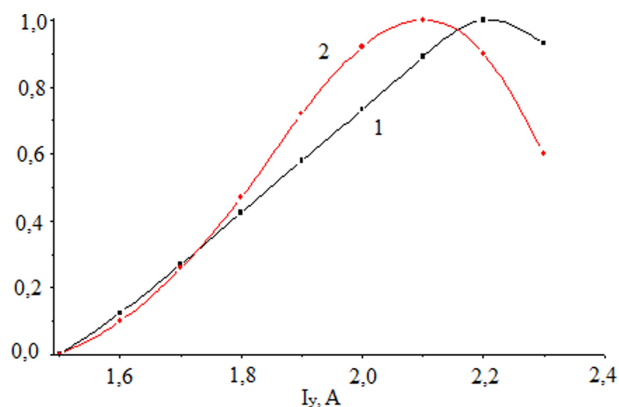

Figure 7. Temperature dependence of ionic current $(CH_3)_2N=CH_2$ during adsorption of imipramine $C_{19}H_{24}N_2$ (m/z 280) (1) and amitriptyline $C_{20}H_{23}N$ (m/z 277) (2) molecules.

slope of the graphs was used to determine the average lifetime of $\tau_i(T)$ or the rate constants of $K_i(T)$ thermal desorption . Using the $\tau_i(T)$ or $K_i(T)$ values obtained from such graphs and the $\beta^* = \dfrac{\Delta I_i}{I_i}$ values obtained from the ratio of the currents of these particles at the current surge maximum, graphs of the dependencies $\ln[K_i(T)\beta^*(T)] = f\left(\dfrac{T}{5040}\right)$ and $\ln[(1-\beta_i(T))K(T)/\beta_i(T)]$, i.e. Arrhenius graphs were plotted.

Using the slope of Arrhenius graphs, the thermal desorption energies of $(CH_3)_2N=CH_2$ radicals during adsorption of imipramine and amitriptyline molecules on the surface of oxidized tungsten, the values of their respective exponential multipliers were determined (Table 1). It is shown that relaxation processes can be approximated by exponential functions, and the decrease in ion current is determined by the kinetics of thermal desorption of ions. The obtained values of rate constants K^+ and activation energy E^+ for the thermal desorption of ions $(CH_3)_2N=CH_2$ with m/z 58 during the adsorption of imipramine and amitriptyline molecules are in good agreement with each other and with the results obtained for the desorption of the same ions during the adsorption of other molecules. However, the obtained SI ionization coefficient β value was not the same for both ions. This small difference in the value of β can be explained as follows: Imipramine has a much lower ionization energy (7.35 eV) than amitriptyline (8.32 eV).[27] This factor directly affects the ionization efficiency of analytes, even for the same radicals using the SI method. Density functional theory (DFT) calculations have been conducted for amitriptyline and imipramine molecules in several studies. For example, Haghdadi studied tricyclic antidepressants such as trimipramine, imipramine, amitriptyline, desipramine, and doxepin using both ab initio (HF/6-

31G(d)) and DFT ((B3LYP/6-31G(d)) and (B3LYP/6-311+G(d)) computations.[28] The author determined molecular geometries and activation energies for ring inversions with full geometry optimizations. It was found that changes in side-chain conformation, the angle value between two phenyl rings, and the type of N-amine on the side-chain can affect drug activity.

Conclusions

From the results obtained for the determination of the lifetime of the FMM particles, it appears that over the entire temperature range of the experiment, the average lifetime $\tau_{MMP} - \dfrac{1}{K_{MMP}}$ determined is 3/5 times higher than the times determined in $VVM \cdot \tau_{MMH} = \dfrac{1}{K_{MMH}}$, the decay of the ion current of the radicals $(CH_3)_2NCH_2^+$ c $m/z = 58$ and in the case of FMM is exponential. This suggests that in this case one of the processes is limiting (either the lifetime of the particles on the surface or the characteristic time of the heterogeneous molecular dissociation reaction on the surface). This indicates that in the experiment, as follows from considered $n_i(t) \sim C\exp[-K_M(T)t] + D\exp[-K_i(T)\cdot t]$, there is the case $I_i(t) \sim n_i(t) \sim C\exp[-K_M(T)\cdot t]$ when $\tau_M >> \tau_i \cdot (K_M << K_i)$.

If we choose the case of a readily ionizable dissociative SI as the adsorbate-adsorbent system, when $(K_M^+ + K_M^0) << K_{Mi}^d$, $K_M \cong K_{Mi}^d$ and $I_i(t) \sim D\exp[-K_M^d(T)t]$. Therefore, in the flow modulation method, the rate of the relaxation process is determined by a slower step in ion formation, and since in both cases the dependence plots ln $\Delta i(t) = f(t)$ are linear, the results obtained in the MMP can be attributed to the value $\tau_d = \dfrac{1}{K_M^d}$ in the adsorbed layer.

The rate constant K^0 and activation energy E^0 of imipramine and amitriptyline molecules were determined by $(C-C)_\beta$ bonding to form ionizable radicals as neutral $(CH_3)_2N=CH_2$ particles.

Acknowledgments

The research doesn't contain the conflict of interest.

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