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13

The mechanism of thermal ionization of methenamine on the surface intermetallic compound NaAux

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Thermal ionization of methenamine ($C_6H_{12}N_4$) on the surface of the $NaAu_x$ intermetallic compound has been studied. It has been established that the processes of decomposition, desorption and ionization of adsorbed compounds, thermally stimulated on the surface, proceed due to the accumulation of energy at the degrees of freedom of the adsorption complex, including the adsorbed compound and a solid, by the mechanism of monomolecular decomposition reactions. In this case, the decomposition of the adsorption complex is accompanied by the desorption of ions that are not in thermal equilibrium with the solid. The uniformity of the temperature dependences of the ion current and their distribution over two groups allowed us to conclude that ions are desorbed from the surface, which correspond to the decays of individual adsorbed molecules, as well as the decays of dimers formed on the surface. The decay of methenamine molecules during thermal ionization occurs in the same way as their decay in vacuum during electron ionization, which indicates the preservation of the bulk structure of methenamine molecules during adsorption and a significant lifetime of the excited state of compounds on $NaAu_x$.

Keywords: thermal ionization, methenamine, intermetallic compound, NaAux.

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Introduction

The interest for study of the thermal ionization (TI) of organic compounds is defined both by practical importance of creation of high sensitive selective detectors, and by the possibility of studying catalytic reactions on the surface of solid bodies [1]. Detectors can be applied for finding traces of various biologically active substances in gas-air mixtures: medicines, food additives, etc. The sensitivity to partial pressure of nitrogen-containing compounds in the gas-air mixture at the atmospheric pressure reaches record-breaking values 10^{-13} Torr [2], which defines the relevance of searching for new materials to create them [3].

In [4] as a material for the emitter of thermal ionization of organic compounds it is proposed to use intermetallic compound $NaAu_x$. The cycle of papers [4,5] shown that the emitter in the form of a gold ribbon with a layer of intermetallic compound $NaAu_x$ created on its surface, in terms of the efficiency of ionization of test nitrogen-containing molecules is comparable with the high-efficient emitters made of oxidized W [3]. The [4] shows the difference of catalytic properties of intermetallic compounds from the metals and oxidized metals — not only decomposition reactions take place on the surface of $NaAu_x$ specific for metals and oxidized metals, but also the association reactions with generation of ions with the weight exceeding the mass of adsorbed compound up to two times. The study of the TI processes of organic compounds on the surface of $NaAu_x$ allows to understand the mechanism of interaction of the organic compounds with the intermetallic compound surface and the nature of its catalytic activity.

TI takes place on the surface of emitter heated up to the temperature of T, which is sufficient in order to prevent superficial accumulation of molecules and products of reactions in the adsorbed layer. In such conditions, at the constant flow of molecules ν and T of the emitter, an equilibrium concentration of adsorbed molecules and compounds formed therefrom is established on the emitter surface. In case of TI on metals and oxides, the adsorbed compounds and products formed with them during the lifetime on the surface get into thermal and charge balance with the emitter. Distribution of ions desorbed from the surface in terms of initial speeds corresponds to the Maxwell's distribution with the emitter temperature [1].

In the overview [1], on the example of amines, the adsorption process and TI of the nitrogen-containing compounds is discussed. It is shown that in case of amines adsorption, a bond with the surface is formed in lone pair electron pair of the atom N on metals and oxides, which results in pulling of electron density from the atom N to the surface and redistribution of electron density in the molecule, as a result of which the β-bonds in the molecule are weakened relative to the atom N. As a result of weakening of such bonds the molecules (M) are decomposing with formation on the surface of $(M-H)$ or $(M-R)$, where R is a hydrocarbon radical, e.g., CH_3 for such compounds as diethyl- and triethylaminamine [6]. Such decompositions are accompanied by formation of a double bond of the atom of carbon with nitrogen, as a result of which N is transformed into the four-valent state, its bond to the surface is weakened, and desorption is facilitated. In addition to (M−H) and (M−R), their dehydrated products are formed on the surface. If as a result of reactions i types of products are formed on the surface, that are desorbed at the flow value ν_i, then, for each of the products desorbed from the surface one can write [1]:

$$\nu_i = \gamma_i(T)\nu, \tag{1}$$

where $\gamma_i(T)$ is individual coefficient for i-th particles depending on the interacting pair adsorbed compound−emitter, that refers to reactions in the adsorbed layer resulting in formation and desorption of i-th particle. For the stationary conditions in case of adsorption of amines on metals and their oxides $\gamma_i(T)$, in general, reflects the dissociative adsorption and desorption of its products according to the mechanism described above. A part of such products is desorbed as ions. For the flows of particles desorbed as charged particles (ν_i^+) and neutral particles (ν_i^0), one may write [1]:

$$\frac{\nu_i^+}{\nu_i^0} = A_i \exp\left(\frac{1}{kT}\left(\varphi - V_i + e(eE)^{1/2}\right)\right), \tag{2}$$

where e is the charge of electron, V_i is potential of ionization of i-th particles, φ is the surface work function, A_i is the ratio of full static amounts for charged and neutral particles, k is the Boltzmann's constant, E is the electric field strength near to the emitter surface.

In case of hydrazines, hydrazones, azids and tetrazenes due to partial hybridization of electrons in the group of nitrogen atoms the redistribution of electron density during adsorption in this series is decreased, as a consequence of which formation of molecular ion $[\mathrm{M}]^+$ and decrease of the formation efficiency of (M−H) and (M−R) are observed [1]. In case of tetramethyltetrazene, $[\mathrm{M}]^+$ only is desorbed from the oxide surface W [7]. In accordance with main TI rules for nitrogen-containing molecules in metals and oxides, provided in [1], in general, the compounds as ions are desorbed from the surface, in which atom N is in four-valence state, and other bonds are chemically saturated, the value $(\varphi - V_i)$ of such compounds at the temperature of emitter must ensure considerable efficiency of ionization according to (2).

The temperature dependencies of the ion currents during TI of organic compounds on oxides W have, in general, a bell-like shape [1,6]. In [8] a bell-like shape of the temperature dependencies of the current of ions was associated with the temperature dependence of specific rate of monomolecular decomposition of adsorbed molecules on the surface $\gamma_i(T)$. For determination of such dependence they used formal description of the theory of monomolecular decomposition in gas [9] with activation of adsorbed molecules due to their interaction with a heated solid body (ion emitter). Activation and deactivation of the molecules occurs at statistically rare high amplitudes of the surface atom oscillations; the surface atom oscillations at medium amplitudes do not participate in the process [10]. Having assumed, that for all decomposition channels $\gamma_i < 1$ and decompositions do not compete with each other, [8,10] proposed the dependence $\gamma_i(T)$ as

$$\begin{aligned}\gamma_i(T) &= \mathrm{const}(E_{ai}/kT)^b \exp(-E_{ai}/kT)\\ &= \mathrm{const}(1/kT)^b \exp(-E_{ai}/kT),\end{aligned} \tag{3}$$

where E_{ai} is the energy of activation of the molecules decomposition with formation of the i-th product, b is the number of active oscillating degrees of freedom in the molecule relative to the disassociation. Hereinafter, the value const includes all parameters independent on the variables in experiments, such as ν, T and E. The density of ion current $j_i(T)$ during TI for i-th product of (1)−(3) in accordance with [8] can be described as

$$\begin{aligned}j_i(T) &= \mathrm{const}\,\nu(1/kT)^b\\ &\times \exp\left(\frac{1}{kT}\left(\varphi - V_i + e(eE)^{1/2}\right) - E_{ai}/kT\right).\end{aligned} \tag{4}$$

In (4) exponential term is responsible for the growth of density of the ion current with the growth T, and pre-exponential term $(1/kT)^b$ is responsible for falling part of the temperature dependence of ion current, which makes such dependence corresponding to the observed bell-like temperature dependences $j_i(T)$. However, the validation of the expression (4) for approximation of temperature dependences of ion currents based on the example of dependence of the current of ions in [8] with the selection of parameters b and E_{ai} indicates repeatability of the experimental data with the expression (4) only near to the ion current maximums (not more than 50% of the maximum current value).

Experimental studies of the dependence $\gamma(T)$ of dissociative adsorption of simple molecules also did not confirm that the expression (3) is true. In [11] for dissociative adsorption of hydrogen on the surface of Cu(111) $\gamma(T)$ was measured within the range of temperatures of metal from 300 to 2000 K. In this range of temperatures γ varies 14 orders of magnitude, meanwhile the dependence $\gamma(T)$ follows the Arrhenius equation for the speed of simple chemical reaction $\gamma(T) = \mathrm{const} \cdot \exp(-E_a/kT)$.

For statistical review of monomolecular decomposition of complex molecules in gas as macroscopic systems, in case of a high frequency of the intermolecular collision (activation and deactivation) it was obtained that specific reaction speed from T is determined by the Arrhenius equation, and the value E_a is determined by the efficient energy of molecules activation [9]. In case of adsorbed molecules it means that their interaction with the surface (activation-deactivation), against the assumption in [10], occurs at a higher frequency corresponding to the frequency of oscillations of adsorbed molecules and oscillations of atoms of the solid body lattice.

For multi-atomic molecules $\gamma(T)$ is exponentially growing as far as T grows, however, a deviation from the Arrhenius equation is observed. For example, for the dissociative adsorption of methane on Pt(111) [12] it is shown that the dependence $\gamma(T)$ measured within the range of five orders of magnitude in the coordinates $\ln(\gamma)$ and $1/kT$ deviates from linear dependence. It might indicate a more complex nature of interaction of adsorbed molecules with the surface, than in the molecules interaction models for gases.

The energy of molecules activation in case of dissociative adsorption, in general, comprises of the energy of molecules before adsorption and the energy transmitted by a heated solid body to adsorbed molecules, and the activated state can be implemented both as disassociation of adsorbed molecules, and their desorption [11,12]. It provides the ground for considering the decomposition of not an individual molecule, but of adsorbed complex including the adsorbed molecule and a solid body. The activated state of adsorbed complex is implemented by two types of decomposition: desorption of molecules and decomposition of molecules with formation of the desorbed products. In case of desorption of organic molecules the activated state could be implemented by a high number of decompositions. The [13] deals with the process of thermal decomposition of methylamine (CH_3NH_2) on Pd(111) and it was established that the adsorbed molecules are disassociated with formation of CH_3NH and H. As a result of methylamine dehydration the bond of molecules with the surfaces via an indefinite pair of electrons of the atom N is transformed into a chemical bond. Due to a heavy adsorption bond the molecules do not desorbed from the surface, due to which their thermal decomposition continues until formation of CN. Then, in accordance with the rules of TI [1] in case of methylamine adsorption no ions desorption should be observed. Analysis of density by the method of functionality [14] shown that in case of thermal disassociation of adsorbed methylamine CH_2NH_2 could be formed on metal at the first step of dehydration. Free bond of carbon of the group CH_2 could result in additional bond of the adsorbed molecule with the surface or to establish the bond with the atom of nitrogen, by transforming it into the four-valence state, typical for TI of amines. In case of formation of the carbon bond with the surface desorption and ionization of dehydrated methylamine is unlikely. In case of formation of double bond of carbon with the atom N the ions $[M-H]^+$ can be desorbed from the surface through the TI mechanism. In case of TI of methylamine on the oxidized rhenium [15] the ions $[M-H]^+$ are desorbed from the surface. It demonstrates that a parallel series of decompositions could occur on the surface and only several of them lead to TI. The activated state of molecules of methylamine could be implemented by deactivation, desorption and three ways of disassociation with formation on the surface of $CH_3{-}NH$ [14], $CH_2{-}NH_2$ and $CH_2{=}NH_2$ [14]. Only $CH_2{=}NH_2$ of three possible decomposition products according to the rules of TI can be desorbed as ions $[M-H]^+$. In this case $\gamma(T)$ of TI (M−H) refers to competition between desorption and disassociation with formation of three possible products.

Efficiency of TI of nitrogen-containing compounds on the surface of intermetallic compound $NaAu_x$ is comparable to oxidized W [4], but the mass-spectrum of their TI on $NaAu_x$ has a higher number of lines versus the mass-spectrum of TI on the surface of metals and oxides of metals [1,4]. A part of the lines in mass-spectra of TI on $NaAu_x$ of nitrogen-containing compounds corresponds to the associating compounds with the mass of up to two times higher than that of the adsorbed compound. In order to determine the differences in formation of the mass-spectra of TI on $NaAu_x$ and on oxidized W a detailed study of TI of tetramethyltetrazene $C_4H_{12}N_4$ (TMT) on $NaAu_x$ was performed [16]. The interest to TMT is explained by the fact that during its TI on the oxidized W only molecular ions are desorbed from the surface [7], and on $NaAu_x$ mass-spectrum includes several dozens of lines, including ions of associating compounds [16].

The [16] established that against the oxidized W on the surface of $NaAu_x$ dissociative adsorption of TMT occurs with TMT decomposition by a double bond of the group of atoms of nitrogen N−N=N−N. As a result of dissociative adsorption of TMT the radicals $(CH_3)_2 = N{-}N$ are formed on the surface. Interaction of these radicals between each other results in formation of heterocyclic compounds, which during desorption from the surface are ionized, by forming the mass-spectrum of TI. As a result, in the mass-spectrum of thermal ionization of TMT there are no molecular ions, as well as ions $[M-H]^+$ and $[M-R]^+$ specific for TI of amines, hydrazines and hydrazones. Temperature dependences of the ion current at thermal ionization of TMT on $NaAu_x$ for various ions have different form: from threshold dependences and rising steadily with the temperature and to bell-like. Such diversity of temperature dependences of the ion current reflects the diversity of reactions in the adsorbed layer.

Methenamine $C_6H_{12}N_4$, the same as tetramethyltetrazene, contains 4 atoms N, but, against „flat“ structure of TMT methenamine is irregular decahedron, whose four vertices include nitrogen atoms. Subject to the spatial structure of molecules one could expect that adsorption of methenamine occurs in the way of establishing the bond to the surface via lone pair of electrons of one the nitrogen atoms, as for the nitrogen-containing compounds [17].

Based on the comparison of mass-spectra and analysis of methenamine decomposition schemes during TI on the emitter made of $NaAu_x$, heated up to $T > 800\,K$, and ionization with electrons in [18] a conclusion is made that methenamine adsorption on $NaAu_x$, against adsorption on TMT, occurs without considerable change of its structure. It allows expecting for less diversity of reactions in the adsorbed layer, than in case of TMT, and enables more detailed study of interaction of the adsorbed molecules with the surface of intermetallic compound $NaAu_x$. For this purpose new detailed studies were performed of the temperature dependences of current formed during TI of methenamine of ions were performed, as well as desorbing ions distribution by kinetic energies was obtained.

1. Experiment

The work was done in the 90-degree sector magnet mass-spectrometer with the radius of 300 mm with double source of ions obtained by thermal ionization (TI) and electron ionization (EI). The ion sources are located along the axis of ions movement from the TI emitter through the EI source to electromagnet. Double source of ions allows to perform analysis of ions desorbing from the emitter based on the kinetic energies by using the method of ion delay curves, as it is presented in [19]. Delaying potential was applied to the electrodes of the EI source for the delay curve method implementation.

Knudsen cell was used for spattering of the sodium atoms flow onto the emitter. Sodium was produced by decomposition of the sodium bichromate mixture with zirconium. A high-vacuum multichannel inlet valves system was used for adding vapors and gases into the mass-spectrometer. Oxygen in the inlet valves system was produced by thermal decomposition of $KMnO_4$. The purity of gas was determined by using the mass-spectrometer and it was 99.99. The study used methenamine produced by PJSC „Metafraks“ of the SV brand with the purity of at least 99.5%. Vacuum training of the methenamine sample by its freezing and heating up under vacuum pumping was performed for dehydration and degasation prior to adding the methenamine into the inlet valves system.

TI emitter in the mass-spectrometer was gold strap with a film of $NaAu_x$ alloy formed on it. Gold strap was cut out of golden foil with the purity of 99.99 and with the size of $0.05 \times 2.5 \times 50$ mm. Prior to the studies the gold strap was annealed for 10 h in vacuum $1 \cdot 10^{-8}$ Torr at $T = 1100$ K, and then for 30 h — in oxygen at $2 \cdot 10^{-6}$ Torr. The layer of $NaAu_x$ was formed *in situ*. Sodium from Knudsen cell was spattered on the gold strap at $T = 1100$ K in order to form film coating of emitter with the layer of $NaAu_x$. Emitter was directly heated up, its temperature within the range of 970−1100 K was measured by means of optical micropyrometer „Pyro“ made by Pyrometer Instrumental Company with the error of less than ±5°. Within the range of 800−970 K the temperature was determined by interpolation of the temperature graduation of the power supplied to the strap, in the range of emitter temperatures of 970−1100 K. The error of determination of the temperature within the range of 800−970 K was ±10 K.

For treatment of the emitter surface from possible contamination with the methenamine decomposition products, oxygen was fed up to the pressure of $1 \cdot 10^{-6}$ Torr together with the inlet of methenamine into the mass-spectrometer. According to results of the experiments, oxygen had not impact to TI of methenamine, but provided treatment of emitter from carbon contaminants. The electrical field strength in the gap between the strap-extraction electrode did not exceed 200 V/cm, which allowed to exclude the impact of the term of sum $e(eE)^{1/2}$ in (2) that did not exceed 0.005 eV, also one may take that the field of stains on the surface having different values φ was not compensated; the surface manifests a uniform efficient value φ in the emission processes [1].

2. Results and discussion

Figure 1 shows mass-spectrum of TI of methenamine on $NaAu_x$ at $T = 860$ K, according to which one can see formation of molecular ions $[M]^+$ with m/z 140 and the absence of mass-lines corresponding to $[M-H]^+$ with m/z 139 and $[M-CH_3]^+$ with m/z 125, which must be principal in the mass-spectrum of nitrogen-containing compounds, according to the results of studies of TI of organic compounds given in the overview [1]. The shape of lines in the mass-spectrum is clearly described by the Gaussian function with the full width of line at 50%, which is the value, e.g., for m/z 58, equal to 0.3.

In accordance with the conclusions [1] on decrease of the role of lone pair of electrons N during adsorption of compounds with the multiple number of atoms N, one may conclude that no significant redistribution of electron density in the methenamine molecules when adsorbing on $NaAu_x$ occurs. At the same time, multiple lines in the TI spectrum indicate the reactions of methenamine in the adsorbed layer that lead to formation of TI products not specific for TI of nitrogen molecules on metals and their oxides.

The [18] established correlation between mass-spectrum of TI of methenamine on $NaAu_x$ at the temperature of emitter $T > 800$ K and mass-spectrum of EI at the energy of electrons of 70 eV. By comparing Fig. 1 and Fig. 2, which represents mass-spectrum of EI of methenamine with the energy of electrons of 70 eV, one can see that the mass-spectra contain $[M]^+$ and the groups of lines near to m/z 126, 112, 96−98, 85, 58 and 42. The same groups of lines were obtained in mass-spectrum of EI of methenamine in [20] with the energy of electrons of 70 eV.

The [21] by using the example of triethylamine performed comparison of the schemes of formation of positive ions

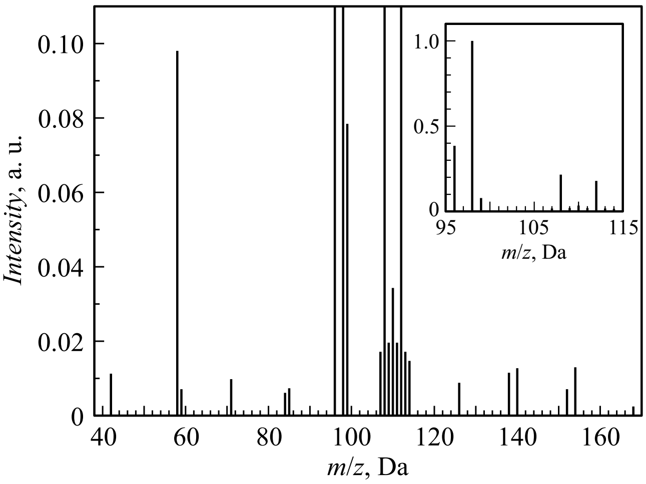

Figure 1. Mass-spectrum of thermal ionization of methenamine. Temperature of emitter is 860 K.

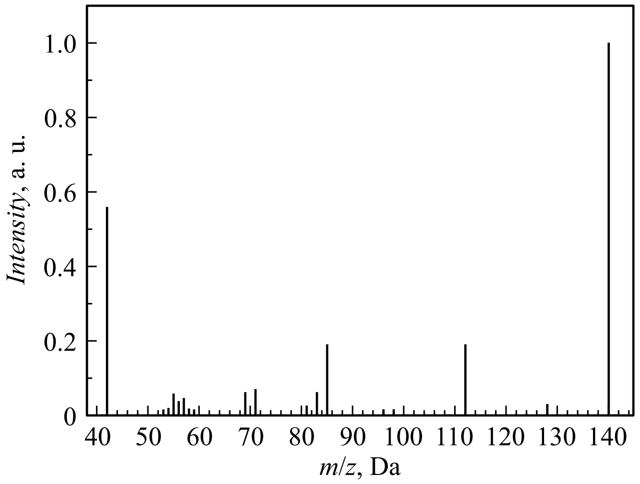

Figure 2. Mass-spectrum of electron ionization of methenamine. The energy of ionizing electrons is 70 eV.

during TI with the temperature of emitter $T > 700\,\mathrm{K}$ [6] and during ionization by electrons with the energy of electrons of 30 eV. As a result of comparison it is shown, that in case of different forms of ionization the compounds undergo the same states of excitation leading to such decompositions. Subject to the conclusions of the study [21], one may assume that methenamine adsorbed on the surface of NaAu_y heated up to the temperature $T > 800\,\mathrm{K}$ undergoes the same decompositions as in case of its excitation during EI with the energy of electrons of 70 eV.

The [20], based on the analysis of mass-spectra of methenamine isotopes, proposed the scheme of formation of the mass-spectrum of EI with the energy of electrons of 70 eV, according to which the methenamine ions $[\mathrm{M}]^+$ are decomposed under the following sequence:

$$1st phase of decomposition: \quad [C_6H_{12}N_4]^+\ (m/z\ 140) \rightarrow [C_5H_{10}N_3]^+\ (m/z\ 112) + CH_2N, \tag{5}$$

$$2nd phase of decomposition: \quad [C_5H_{10}N_3]^+\ (m/z\ 112) \rightarrow [C_4H_9N_2]^+\ (m/z\ 85) + CHN, \tag{6}$$

$$3rd phase of decomposition: \quad [C_4H_9N_2]^+\ (m/z\ 85) \rightarrow [C_2H_4N]^+\ (m/z\ 42) + C_2H_4NH. \tag{7}$$

As a result of such decompositions ions that contain nitrogen atoms in the four-valence state are formed. The decomposition products valencies are saturated. At the same time, ions formed at the phases 1 and 2 of decompositions preserve the 3D structure. In the mass-spectrum of TI of methenamine one also may observe ions with m/z 140, 112, 85 and 42.

The energy of electrons during EI is enough for ionization of the molecules and for excitation of them. There are no collisions of excited molecules with other particles in the vacuum, as a result of which the excitation energy is preserved in the decomposition products, this providing the sequence of decompositions proposed in [20]. As shown above, monomolecular decomposition on the surface occurs at a high frequency of interactions between the adsorbed compound and the surface, i.e. exchange of the energy between adsorbed compound and solid body (activation and deactivation of molecules) occurs at a higher frequency. The activated state of the adsorption complex leads either to desorption of the molecule or to decomposition of the molecule with formation of adsorption complexes by the decomposition products. The adsorption complexes formed by the decomposition products at a high frequency of interactions with solid body cannot preserve the activation energy of the decomposition originating them. This is why in contrast to the decompositions in the vacuum each stage of decomposition on the surface must be considered as the decomposition of the adsorption complex of each product of initial decomposition. One may assume that ions $[\mathrm{M}]^+$ are desorbed from the surface and their further decompositions occur beyond the surface in accordance with the sequence of decompositions proposed in [20] due to the energy reserved on the surface. Ions formed beyond the surface as a result of decomposition of initial ions are fragment ions. In case of decompositions of initial ions, the fragment ions in the area of acceleration by the electrical field of the ion source are registered as the lines extended in direction of lower masses, and in case of decompositions within the spaces without field of the mass-spectrometer — as diffusion lines with fraction indicator of mass and the width at the 50% of several masses [1,6]. Since all intensive lines in the mass-spectrum are narrow and clearly described by the Gaussian function, it means, that the mass-spectrum of TI of methenamine on NaAu_x consists of initial ions corresponding to the compounds originating from the reactions on the surface and being ionized during desorption process. Based on the foregoing one could expect that the temperature dependences of the current of ions formed as a result of the decomposition of the methenamine adsorption complex and that of its decomposition products will be different. A series of publications of studies of TI of organic compounds on oxides W, e.g. [22], it is taken that the value γ_i has a low dependence on T, thus allowing to determine the value of $(\varphi - V_i)$ from (2) by the temperature dependences of ion currents.

Figure 3 shows dependence of the current of molecular ions of methenamine $[\mathrm{M}]^+$ on the temperature of emitter, according to which it can be seen that up to $T = 870\,\mathrm{K}$ as far as T is growing the ion current is increased, and then its weak falling is observed. The form of such dependence is similar to the temperature dependences for so called „slight ionization" $(V < \varphi)$ [1,23]. Initial growth of the ion current for „slight ionization" is related with the growth in case of decrease of the surface coating with adsorbed compounds with the growth of T [23]. In the process of increase with the growth of T the emitter temperature $T_{\max}$ is achieved,

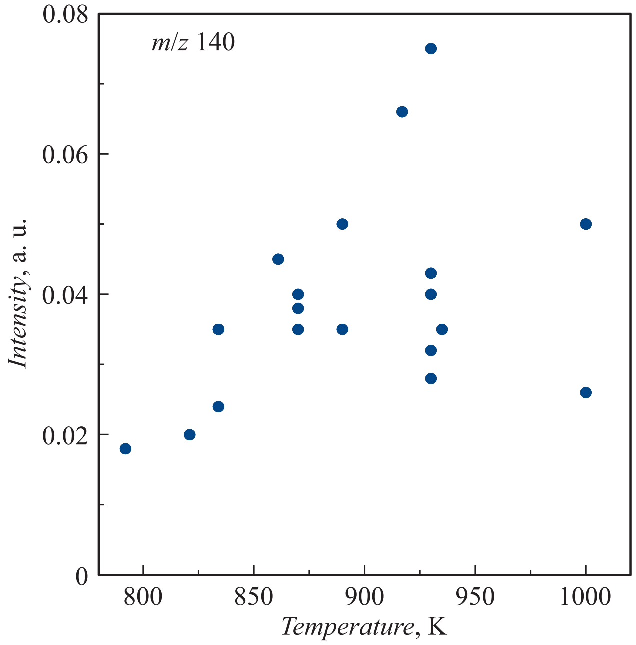

Figure 3. The dependence of the current of molecular ions of methenamine $[\mathrm{M}]^+$ on the temperature.

at which $\varphi(T) = V$, and further growth of φ in accordance with (2) leads to decrease of the ion current. Moreover, at $\varphi > V$ according to (2) the efficiency of ionization is decreased as far as T is growing. If the temperature dependence of molecular ion current of methenamine $[\mathrm{M}]^+$ correlates with the case of „slight ionization“, then the value φ of the surface NaAu_x must be higher than the potential of ionization of methenamine $V = 8.5\,\mathrm{eV}$ [24], i.e. $\varphi > 8.5\,\mathrm{eV}$. In [18] by the full current method the value of the work function of NaAu_x was estimated as 7.6–7.9 eV. At the same time, for all known emitters the values of the work function do not exceed 7 eV [25]. The cause of overestimation of φ from (2) will be discussed below.

By assuming that the temperature dependence of the current of ions is determined not only by the efficiency of ionization according to (2), let's consider the processes that could have impact thereto. For the adsorbed molecules we consider desorption and disassociation of molecules as reactions of monomolecular decomposition of the adsorption complex. Under stationary conditions a part of adsorption complexes on the surface of emitter with the temperature of T is transformed to the activated state at the rate of K_0, which can be deactivated at the rate of K_1. At the rate of K_2 molecules could be desorbed at the rate of K_3 — dissociate to form of $\mathrm{C_5H_{10}N_3}$ in accordance with the first phase (5) and desorption of the disassociation product; at the rate of K_4 — dissociate adsorption of $\mathrm{C_5H_{10}N_3}$ on the surface; at the rate of K_5 — dissociate to form of compounds not considered in the scheme of decompositions (5) and their desorption from the surface; at the rate of K_6 — dissociate to form of compounds not considered in the scheme of decompositions (5), with adsorption on the surface.

According to the theory of monomolecular decomposition [9], only activated compounds participate in the decomposition reactions, i.e. those compounds that have internal energy exceeding the efficient energy of the reaction. In stationary conditions at $T = \mathrm{const}$ relative number of molecules of methenamine as a part of activated complexes N^*/N is determined by the ratio of the rates of activation and deactivation K_0 and K_1. The number of methenamine molecules supplied per the unit of time is equal to the sum of molecules deactivating, desorbing and decomposing via different channels, i.e. $\nu = \mathrm{N}\sum K_i$, where i is integer number, that varies from 1 to 6 in the case in question. The equation (1) can be restated in the form $\nu_i = \nu(K_i/\sum K_i)$. Subject to (2), the following can be written for the density of the ion current at $V_i > \varphi$

$$j_i(T) = \mathrm{const}\,\nu\left(K_i/\sum K_i\right)\exp\left((\varphi - V_i)/kT\right). \qquad (8)$$

$K_i(T)$, as it is considered above, — the functions exponentially growing with the temperature, which can be approximated by the Arrhenius equation, and, therefore, the function $K_i/\sum K_i$ is descending with the growth of T, if several channels are available. During TI of diethyl- and triethylamine on oxidized W [6], after reaching by the emitter of the temperature, which is sufficient for activation of formation and desorption (M–H), the ion current $[\mathrm{M{-}H}]^+$ is growing with the temperature according to (8). Activation of the second decomposition channel with formation of $(\mathrm{M{-}CH_3})$ increases $\sum K_i(T)$, which leads to falling of the current $[\mathrm{M{-}H}]^+$. As a result, the temperature dependence of the current of ions $[\mathrm{M{-}H}]^+$ has a bell-like shape [6,8].

Initial growth of the current of molecular ions of methenamine $[\mathrm{M}]^+$ with T as per (8) is related with the increase of efficiency of formation, desorption and ionization of molecules. Once the emitter achieves the temperature $T_{\max} = 870\,\mathrm{K}$, certain channels of the methenamine molecules decomposition are activated, which leads to stop of the current growth and its further falling.

Decomposition of methenamine ions during its EI at the first phase (5) leads to formation of $[\mathrm{C_5H_{10}N_3}]^+$ (m/z 112). During TI of methenamine, as it can be seen in Fig. 1, the ions with m/z from 107 to 114 are registered together with the ions with m/z 112. Formation of that group of ions occurs during decomposition of the adsorbed methenamine, the same as during decomposition of the methenamine ion during EI. Based on the results of the studies [20], the scheme of decompositions of methenamine is made, as shown in Fig. 4, with formation of compounds, which form principal mass-lines of that group of ions during TI. As it can be seen in Fig. 4, formation of these compounds occurs in case of rupture of three bonds in the methenamine molecule. The decomposition products are differed by the distribution of atoms H among them. Nitrogen atom in

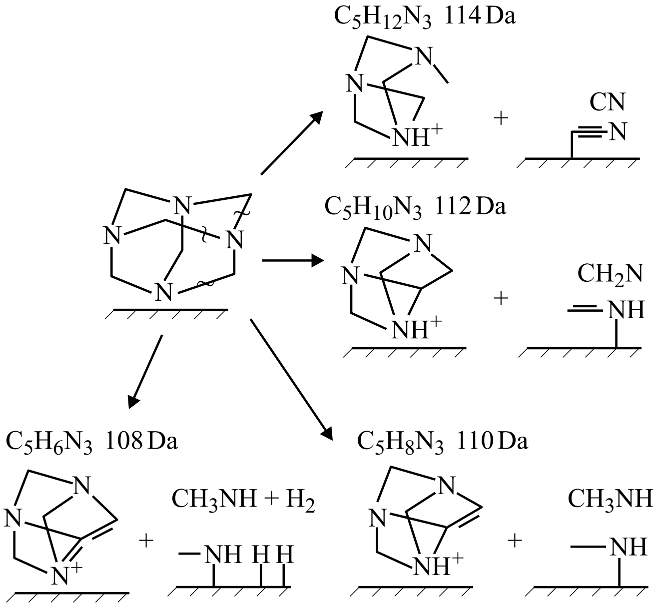

Figure 4. Scheme of compounds formation on the surface of $NaAu_x$, leading to formation of ions with m/z 108, 110, 112 and 114.

ionized products of decomposition is in the four-valence state; chemical bonds are saturated.

The temperature dependences of the current of ions of the most intensive mass-lines of that group of ions with m/z 108, 110 and 112 are shown in Fig. 5. It can be seen that these dependences are similar, that confirms the conclusions of the study [26] as to similarity of the temperature dependences of the ion current during TI of the decomposition products differed by the number of hydrogen atoms. The form of temperature dependences of the current of ions with m/z 108, 110 and 112 by its shape corresponds to the temperature dependence of the current $[M]^+$. Based on the comparison of Figs. 3 and 5 one can see that the temperature of the start of the registration of the current of ions with m/z 108, 110 and 112 is higher than that of the molecular ions, and it is $T = 820\,K$. The initial growth of the current of the group of ions with m/z 108, 110 and 112 as far as T of emitter is increased, according to (8) is related with the increase of efficiency of formation and desorption $K_3(T)$, as well as with increase of efficiency of ionization of the desorbed compounds. Upon reaching the temperature of emitter of $T_{\max} = 920\,K$ the current growth stops, and at $T > T_{\max}$ the ion current starts falling with further growth of T. Based on the comparison of Figs. 3 and 5 one can see that the values $T_{\max}$ for the current of that group of ions are higher than that for the molecular ions. The causes of differences between such temperature will be discussed below. The temperature dependences of the current of ions of that group with m/z 107 and 114, not shown in Fig. 5, correspond to such of the ions with m/z 108, 110 and 112.

Other group of ions in the mass-spectrum of TI of methenamine has the $m/z\ of$, 96 and 98. Though this group of ions is registered in the mass-spectrum of EI, its formation is not discussed in [20]. However, we assume that the decomposition occurs under the same scheme as the decomposition in question with formation of ions with m/z 108, 110 and 112 due to breaking of three bonds in the methenamine molecule, as shown in Fig. 6.

Figure 5 shows temperature dependences of the current of ions with m/z 96 and 98. These are similar to each other, which confirms a common mechanism of their formation. The form of temperature dependences of that group is similar to that of the temperature dependences of molecular ions and ions of the group with m/z 107–114. At the same time, the temperatures of the start of the registration of the current and $T_{\max}$ for ions with m/z 96 and 98 are similar to such for the molecular ions, and lower, than for the group of ions with m/z 107–114.

In accordance with the methenamine ions decomposition sequence proposed in [20], during EI at the second phase the ion with m/z 112 is decomposed with formation of the ion $[C_4H_9N_2]^+$ with m/z 85, as shown in the equation (6). As it can be seen from the structure of the compound $C_5H_{10}N_3$ (112 Da) in Fig. 4, formation of the compound $C_4H_9N_2$ (85 Da) occurs when three bonds are broken and separation of CHN.

Formation of relatively intensive mass-line with m/z 58 was not considered in the study [20]. By assuming preservation of the decomposition sequence, one may assume that the compound ionizing with m/z 58 is formed as a result of decomposition of $C_4H_9N_2$ (85 Da) following rupture of three bonds and separation of CHN. At the third phase of decomposition of the methenamine ions during its EI, in accordance with equation (7), the compound C_2H_4N is formed, which may form ions with m/z 42 during TI. This line is observed in the mass-spectrum of TI of methenamine, as it can be seen in Fig. 1, which confirms possibility of that decomposition on the surface.

The temperature dependences of the current of ions with m/z 42, 58 and 85 are similar to the temperature dependences of the current of the group of ions with m/z 107–114, given for principal ions in Fig. 5. They have similar temperatures of the start of the registration and $T_{\max}$, which confirms their common origin and correctness of the scheme of methenamine ions decomposition proposed in [20]. At the same time, the form of mass-lines of such ions indicates that these are desorbed from the surface, but not formed from the ions with m/z 112 beyond the surface.

In the mass-spectrum of TI of the methenamine (Fig. 1) the lines are registered that are absent in the mass-spectrum of EI, namely the lines with m/z 138, 152, 154 and 168. Registration of ions corresponding to the compounds with the mass higher than that of the methenamine molecules (140 Da) indicates formation of associating compounds on the surface. The possibility of association reactions between the co-adsorbed organic compounds was noted in [27]. The mechanism of their formation refers to the establishment

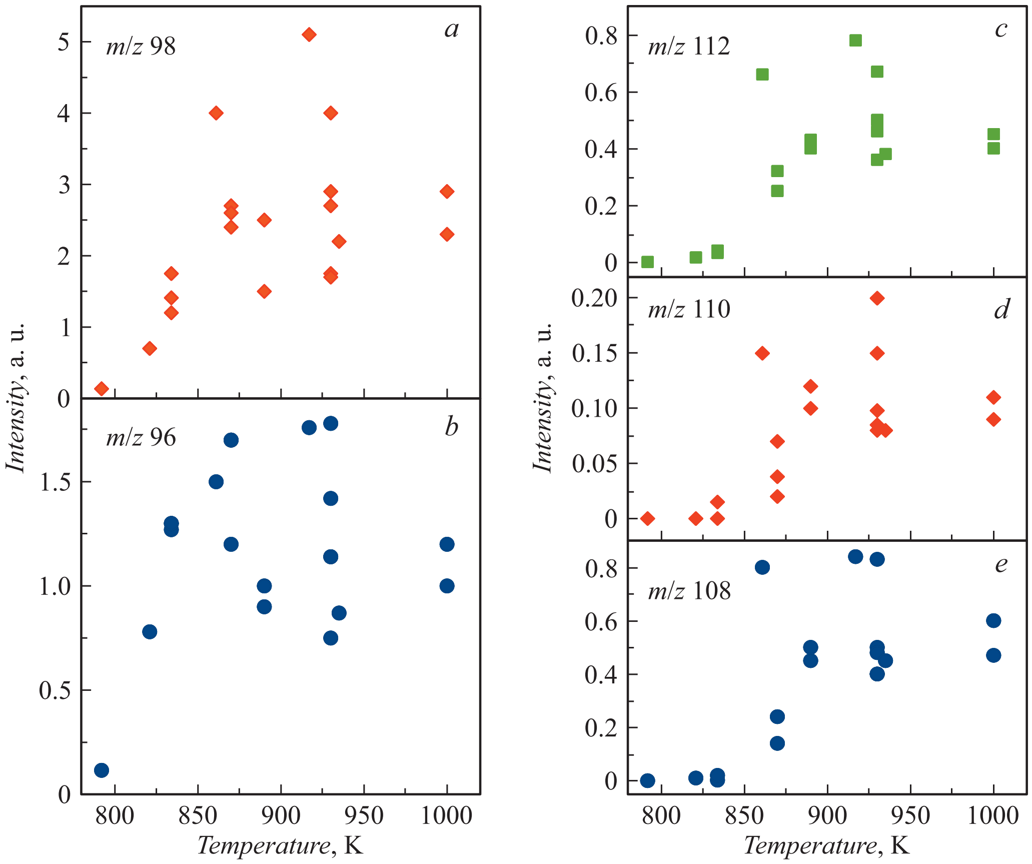

Figure 5. Temperature dependences of ions with m/z 96 (b), 98 (a), 108 (c), 110 (d) and 112 (e).

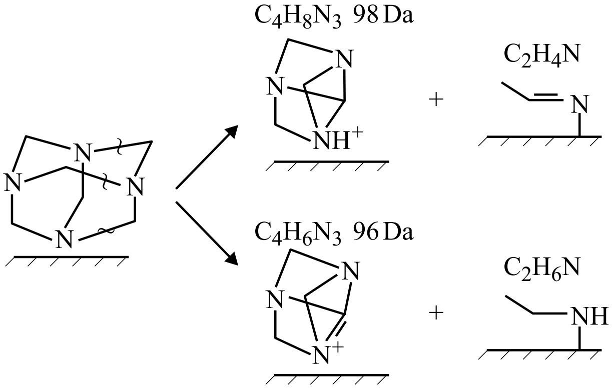

Figure 6. Scheme of compounds formation on the surface of $NaAu_x$, leading to formation of ions with m/z 96 and 98.

of hydrogen bond between co-adsorbed molecules, which can be transformed into chemical bond [6,28,29]. Decomposition of dimers of adsorbed molecules results in their hydration [6,28] and methylation [18,29]. Figure 7 shows formation of methenamine dimers and their several possible decompositions with formation of ions with m/z 108, 126, 138, 140, 154 and 168. Ions with m/z 152 are formed in the same way as the ions with m/z 154, but with C=C bond of the attached methylene group. Formation of dimers indicates that the life time of the methenamine molecules adsorbed on the surface is high enough to efficiently form dimers.

Temperature dependences of the current of ions with m/z 106, 108, 126, 138, 140, 152, 154 and 168 are similar to each other. Such dependences have similar temperature values of the current registration start and $T_{\max}$. It indicates to a common mechanism of their origination. Other group of ions with m/z 114–107, 85, 58 and 42 has higher values of the current registration start temperature and $T_{\max}$. Subdivision of ions by temperature dependences of the ion currents into two groups allows to assume that the first group (low temperature) is related with the dimers decomposition, and the second group (higher temperature) — with the decomposition of individual methenamine molecules. In each group the ionizing compounds differ by the mass up to several times and by the composition, accordingly,

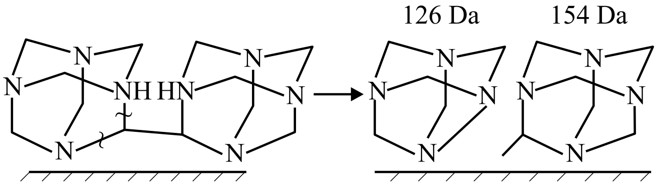

Figure 7. Methenamine dimers formation scheme.

as well as by the structure from „three-dimensional“ to „flat“. Such differences of compounds must lead to their different physical and chemical characteristics, including the difference of values K_i and V_i. In accordance with the equation (8) it must be manifested as the difference of temperature dependences, as it was observed for TI on metals and their oxides [1]. The temperature dependences of the ion current within the group are similar, regardless of the differences in their physical and chemical characteristics. It indicates that the equations (2) and (8) do not reflect the observed process of TI of methenamine on NaAu_x. It may be assumed that the temperature dependences of the ion current reflect the dependence of the efficiency of decomposition of adsorption complexes on the emitter temperature.

Activated complexes, once enough energy is accumulated on the bond, are decomposed with desorption of the products, including in the form of ions. During decomposition of the adsorption complex all products are formed, that are typical for this decomposition, having similar temperature dependences and registered in the mass-spectrum. It means that the products of such decompositions are not adsorbed on the surface. Initial growth of the ions current with T in two groups of ions reflects increase of the energy of adsorption complexes as far as the emitter temperature is growing. Falling of the ions current at $T > T_{\max}$ indicates the start of decompositions of the complexes with formation of the products not being ionized during the desorption. It is known, that within the range of temperatures 970–1300 K methenamine is decomposed with release of not ionized compounds H_2, CH_4, C_2H_2, C_2H_4 and C_2H_6 [30]. Coincidence of the sequence of decompositions of the methenamine molecules during EI and TI and similarity of the temperature dependences within the group of ions with m/z 114–107, 85, 58 and 42 could indicate that in one act of decomposition of the activated adsorption complex of methenamine the whole sequence of the decompositions occurs, and the life time of the energy of the complex activation is enough for these processes to flow. The coincidence of the products during EI and decomposition of the adsorption complex means that these products are stable and their formation is beneficial in terms of the energy.

Dimers and adsorption complexes associated therewith could have at the $3n - 6$ degrees of freedom, where n is the number of atoms in the complex, the reserve of energy, which is higher than the methenamine molecules and the complexes associated therewith [9]. Because of this, the group of ions with m/z 106, 108, 126, 138, 140, 154 and 168, related with the decomposition of dimers, has lower values of the current registration start temperature and $T_{\max}$, than that of the molecule.

The establishment of thermal and charge balance between a solid body and the organic compounds adsorbed on it [1] is typical for the emitters made of metals and oxides; the distribution by kinetic energy of the ions desorbing from the surface corresponds to the Maxwell's distribution at the emitter temperature [1,22]. If during decomposition of the adsorption complexes, the decomposition products are not adsorbed on the surface, but desorbed due to transition to the repulsive sector of the potential curve, then no thermal balance between the desorbing products of decomposition and a solid body is established. In order to determine the presence or absence of thermal balance between the methenamine decomposition products and intermetallic compound NaAu_x, the study of the distribution by kinetic energy of ions desorbing from the surface was performed. It was performed by the delay curve method by applying of delaying potential onto the EI source electrodes, as it is shown in [19]. Figure 8 shows typical logarithmical dependence $\ln(I)$ of the ions current with m/z 98 on the delaying potential. The accelerating potential in the source of TI was $V = 1000$ V; the delaying potential varied within the range of 1004–1005 V, which considered the contact difference of potentials of the emitter and EI source electrodes, to which the delaying potential was applied. The emitter temperature was 930 K. The error of determination of the emitter temperature did not exceed 10 degrees.

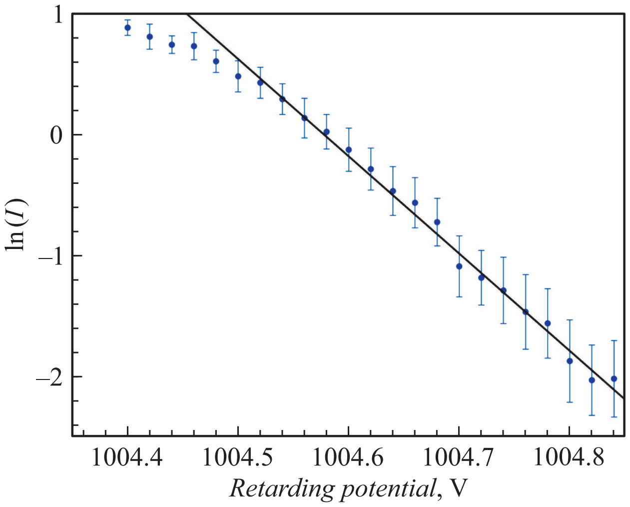

Figure 8. Logarithmical dependence $\ln(I)$ of the current of ions with m/z 98 on the value of the delaying potential. T of emitter is 930 K. Straight line is the linear approximation of the dependence $\ln(I)$ on T.

The slope of the straight line in Fig. 8, according to [19,31], is determined as $a = -1/kT_{\mathrm{MD}}$ and corresponds to the temperature of the Maxwell's distribution by kinetic energy of the ions desorbing from the surface. The value T_{MD} of ions with m/z 98 at the accelerating field 1000 V was $T_{\mathrm{MD}} = 1350$ K, which is considerably different from the temperature of the emitter $T = 930$ K. The error of determination of slope of the straight line sector of the delay curve „a“ is lower than one percent, i.e. determination of the temperature from $a = 1/kT$ will be (1350 ± 15) K. The temperature of the Maxwell's distribution by the kinetic energy T_{MD} is 420 K higher than that of the emitter. It indicates that ions are desorbed from the surface without reaching the thermal balance with the emitter. TI of methenamine on the surface of $NaAu_x$ is non-equilibrium process, therefore, the expression (2) is not applicable. However, by using the temperature T_{MD} instead of the emitter temperature for determination of φ by the full current method, for the molecular ions as per (2) we obtain $\varphi = 6.2{-}6.5\,\text{eV}$, 1.4 eV lower than the estimate in the study [18]. This value of the surface work function corresponds to the values φ for known emitters [1,25].

Non-conformance of T_{MD} to the emitter temperature indicates that during decomposition of activated adsorption complex on the surface $NaAu_x$ the desorption and ionization of particles occurs during decomposition of the complex without adsorption of the decomposition product on the surface. The energy accumulated at the degrees of freedom of the complex is enough for rupture of the bonds, desorption and ionization of the products. This mechanism ensures a high efficiency of ionization and results in overestimation of the value of the work function, when it is determined by the full current method.

Conclusion

The results of the study have shown that the theory of TI of organic compounds given in the overview [1], does not provide a full description of ions formation during methenamine adsorption on the surface of a heated up solid body (intermetallic compound $NaAu_x$). The life time of the methenamine molecules on the surface is enough for efficient formation of the methenamine dimers. By the temperature dependences of the ion current it was established that the observed ions can be subdivided into a group of ions formed during TI of the methenamine molecules, and into a group of ions formed during TI of the methenamine dimers. The temperature of the Maxwell's distribution by kinetic energy of ions desorbing from the surface exceeds the emitter temperature, which indicates the non-equilibrium process. The assumption was considered that the adsorbed molecules and their dimers form adsorption complexes with the surface, which, due to the energy accumulated in them, are decomposed with desorption of ions. In the process of decomposition of complexes the sequence of the methenamine molecules decompositions is implemented as observed during electron ionization of molecules in the vacuum. With that, the products formed during decomposition of adsorption complexes are desorbed without adsorption on the surface. The temperature dependences of methenamine ion currents and products of methenamine reactions on the surface are determined by the temperature dependence of activation of corresponding adsorption complexes.

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Conflict of interest

The authors declare that they have no conflict of interest.

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