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Surface Ionization Mass Spectrometry of Imidacloprid and Chlordimeform on Oxidized and Metallic Tungsten Surfaces

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Abstract : In this work, we have studied the synthetic insecticides imidacloprid and chlordimeform on both oxidized and metallic tungsten thermoemitters in electric fields of $E<10^5$ V/cm using surface (thermal) ionization mass spectrometry. Imidacloprid (1-(6-chloro-3-pyridylmethyl)-N-nitroimidazol-2-ylideneamine) is a neurotoxic insecticide of the neonicotinoid family and is one of the most widely used in agriculture. Chlordimeform is a carboxamidine, classified as both a formamidine insecticide and acaricide, as well as a member of monochlorobenzenes. The experiments were conducted using the MI 1201 B magnetic static mass spectrometer, which was specifically modified for the surface ionization method. The studied samples were efficiently ionized on the oxidized thermoemitter, and the mass spectra consisted of M^+, $[M\text{-}H]^+$, $[M\text{-}H\text{-}2nH]^+$ and $[M\text{-}R]^+$ ions. On the metallic thermoemitter, the mass spectra consisted of fewer lines compared to those obtained on the oxidized surface, indicating that no additional ions were generated. The mechanisms of ion formation on both oxide and metallic surfaces were discussed. For the first time, the ionization energies of the major ions of the studied compounds were evaluated using the surface ionization method, as well as the heat of sublimation of the molecules. Unimolecular decays were detected in the mass spectrum of chlordimeform. The surface ionization mass spectrometry data of samples was compared with the gas chromatography-mass spectrometry data.

Keywords : Surface ionization mass spectrometry, metallic and oxidized thermoemitter, imidacloprid and chlordimeform, adsorption, ion formation, gas chromatography-mass spectrometry

Introduction

Imidacloprid is a synthetic neurotoxic insecticide from the neonicotinoid family and it is among of the most widely used in agriculture. However, imidacloprid can cause health issues in humans, such as cancer, chronic kidney disease, neurological disorders, and reproductive problems. Chlordimeform is a carboxamidine, a formamidine insecticide, a formamidine acaricide, and a member of the monochlorobenzenes. Due to its carcinogenic potential, chlordimeform has been banned in several countries for agricultural use. These insecticides, therefore, attract significant interest from researchers. Mass spectrometer is one of the most powerful tools available for studying such compounds. Until now, these pesticides have been analyzed in various objects using several mass spectrometry ionization methods, as well as chromatography coupled with mass spectrometry techniques, such as electron ionization (EI), atmospheric pressure chemical ionization (APCI), electrospray ionization (ESI), gas chromatography-mass spectrometry (GC-MS), high performance-liquid chromatography mass spectrometry (HPLC-MS), thermal desorption electrospray ionization mass spectrometry (TD-ESI/MS), gas chromatography–tandem mass spectrometry (GC–MS/MS) and ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS).[1-10] These studies demonstrate that pesticides in various matrices are primarily investigated using chromatography techniques coupled with mass spectrometry. However, developed direct methods have limitations, such as matrix effects and selectivity. Therefore, the development of sensitive, direct, and selective ionization methods remains an urgent task in this field.

The surface ionization (SI) method is one of the promising techniques for this purpose. The SI phenomenon is a

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thermally equilibrium process, where the evaporating particles (both ions and neutrals) exhibit Boltzmann energy distributions at a temperature equal to that of the solid, T. The SI of organic compounds involves the formation of positive or negative polyatomic ions during the thermodesorption of particles from the solid surface and depends on the probability of isoenergetic electron exchange between the particle and the solid. The method has a high selectivity to the ionization potential of the substances. For example, if the ionization potentials of two compounds differ by 1 eV, their ionization efficiency by surface ionization can vary by up to 10^5 times. Rasulev et al. first reported of the applicability the SI method to organic compounds.[11] Until now, many organic and bioorganic compounds have been studied using an electric field not exceeding 10^5 V/cm, and their SI regularities have been established by the method.[12-24] It was found that the SI is a highly selective and efficient method for ionizing nitrogenous bases. Amines, hydrazines and their derivatives have been studied using the SI/MS method and the main regularities of SI in different classes of organic compounds have been identified, enabling the prediction of ion composition and their current densities.[11] SI methods have been developed to determine the properties of ionizable polyatomic particles (ionization potentials of radicals and complexes, binding energies in ions) and their interaction characteristics with surfaces (adhesion coefficients to surfaces, rate constants, and activation energies of thermal desorption of polyatomic particles and heterogeneous dissociation reactions). Highly sensitive and selective methods and instruments have been developed for the detection and analysis of trace amounts of physiologically active nitrogenous bases, opening a new direction in gas analytical instrumentation.[11,25] In our previous works, we demonstrated that SI/MS could be applied for the direct detection (without preliminary chromatographic separation) of omnoponum that consists of five alkaloids of opium, as well as for morphine and narcotic stimulants in biosamples.[21-23]

In this work, we studied imidacloprid and chlordimeform using the SI/MS method with oxidized and metallic tungsten thermoemitters. The aim of this study was to elucidate the SI characteristics of these molecules on different thermoemitters such as ion composition, main ions of these compounds, temperature behavior of formed ions, heat of sublimation and ionization energy in order to expand the analytical capabilities of this method for future applications to these compounds. The SI/MS data were compared with GC-MS data for validation.

Experimental

Chemicals and samples

Ethanol (HPLC grade) was purchased from Fortek, distributor company (VWR International S.A.S, France). Chromatographic grade samples of imidacloprid ($C_9H_{10}ClN_5O_2$) and chlordimeform ($C_{10}H_{13}ClN_2$) were obtained from Sigma-Aldrich company. The samples were diluted in pure ethanol concentration of 1 mg/ml. For SI/MS analysis, a special quartz evaporator was filled with 2-8 μL of the solution and dried at room temperature in the open air before being subjected to analysis.

Mass spectrometers

The experiments were conducted using a MI-1201B static magnetic mass spectrometer (“Electron”, Sumi, Ukraine) that was upgraded for SI research. An oxidized and metallic textured tungsten ribbon (1 mm × 12 mm × 0.02 mm) was used as a thermoemitter. Prior to oxidation, the tungsten ribbon underwent texturization by being heated in a vacuum at a pressure of 1×10^{-6} Pa. An alternating current was passed through the ribbon for 2 hours at T = 2000 K, followed by an additional 30-40 minutes at T = 2500 K.[26] A similar procedure was also performed for the new metallic thermoemitter. The oxidation procedure has been described in detail elsewhere.[37] Oxidation of the tungsten ribbon was carried out at a temperature of 1000 K and a pressure of 1-2 Torr. The radiation emissivity coefficient (ε_λ) was monitored throughout the process. When ε_λ stopped changing, the temperature was increased to 1100 K, and oxidation continued for another 10 minutes. The heater current was slowly reduced. The total oxidation time was approximately 30-40 minutes. The thermoemitter was heated using a stabilized DC power supply unit with smooth current regulation in both directions. The pulling electrode of the ion source was powered by a separate DC supply. The operating vacuum ranged from 1.0 to 3.0×10^{-6} Pa. The mass spectrometer was operated in positive ion mode, with the electric field (E) at the thermoemitter surface not exceeding 10^5 V/sm. Ion detection was performed using a secondary electron multiplier. Molecular flows of the studied samples were directed to the thermoemitter surface using a special quartz evaporator mounted in the ionization chamber. The evaporator temperature (t_{evap}) varied within the range of 303 – 403 K, while the thermoemitter temperature was regulated within a range of T_{em} = 500–1250 K for oxidized thermoemitter and up to 2100 K for metallic thermoemitter.

GC-MS conditions

GC-MS analysis was performed on an Agilent 7890B gas chromatograph (GC) coupled with an Agilent 5977A quadrupole mass spectrometer (inert MSD with Triple-Axis Detector, USA). The transfer line temperature was set to 280°C. Electron ionization (EI) was carried out at 70 eV energy, with an ion source temperature of 250°C. The quadrupole temperature was maintained at 150°C. The mass spectrometer was operated in full scan and single ion monitoring modes.

A 1 μL sample was injected at an injector temperature of 280°C. The carrier gas used was hydrogen, introduced at a flow rate of 1.25 mL/min, generated by a Hydrogen generator (Hydrogen, Peak Scientific Instruments, Scotland, UK). Separation was performed on an HP-5MS 5% phenyl methyl silox capillary column (length: 30 m, internal diameter: 0.25 mm, film thickness: 0.25 µm, USA). The oven temperature was held at 150°C for 1 min, followed by a ramp 15°C/min to 300°C.

Results and Discussion

Imidacloprid

As previously mentioned, organic compounds containing nitrogen bases are effectively ionized by the SI/MS method. Many pesticides, including imidacloprid are nitrogen-containing bases. Therefore, it was expected that imidacloprid molecule should be efficiently ionized by the SI/MS method. Imidacloprid was first studied using an oxidized tungsten thermoemitter by the SI/MS method. It is known that the oxidation process increases a work function *(φ)* of the metallic thermoemitter.[11] Usually, metallic tungsten band has the work function of 4.6 eV and the oxidizing it led to increase work function to 6.5 eV.[26] Figure 1a shows a SI mass spectrum of imidacloprid obtained on the oxidized tungsten thermoemitter. It was obtained at thermoemitter temperature of 1200 K and an evaporator temperature at 345 K. The mass spectrum consists of a molecular ion M^+ at *m/z* 255 and fragment ions. These molecules and fragments have relatively long lifetimes, achieving thermal and charged equilibrium on the thermoemitter surface before ionization through the SI mechanism, which has shown measurements of their average lifetime on the thermoemitter surface.[11] Measurable currents of molecular ions M^+ can be observed when the ionization energies of molecules do not exceed the thermoemitter work function by more than ~2 eV. Additionally, the molecules should not undergo complete transformation into particles of different chemical compositions during their lifetime in the adsorbed state. Even under these conditions, M^+ ions are easier to detect in compounds that do not form $[M\text{-}H]^+$ ions, as the isotopic current of these ions can interfere with the M^+ ion current in mass spectrometers of conventional resolution. The base peak in the mass spectrum corresponds to an ion at *m/z* 194. The other ion lines result from deep fragmentation of the adsorbed molecule on the hot surface. Imidacloprid was effectively ionized by SI/MS, with the current density (*j*) of the main ion (*m/z* 194) being approximately 10^{-9} A/cm^2. Most of these ions have saturated bonds and non-shared electrons. They are represented as ions with the a positively charged quadrivalent nitrogen atom with the sp^2-hybrid orbitals. A radical ion at *m/z* 185 was also observed in the mass spectrum. When nitrogen-containing molecules are adsorbed, ions with even or odd mass are formed depending on the number of nitrogen atoms, according to the nitrogen rule.

Imidacloprid was then analyzed using a metal tungsten thermoemitter. Figure 1b shows the SI mass spectrum obtained at a thermoemitter temperature of 2000 K and an evaporator temperature of 345 K. Mass spectrum consists of a few fragment ions at *m/z* 194, 196, 168, 166, 160, 126, 72, and 58 compared to those obtained for the oxidized thermoemitter. Ion with *m/z* 194 was also a major peak in the mass spectrum and its current density was approximately 10^{-12} A/cm². As previously stated, the SI method is highly selective based on the ionization energy of compounds. If the work function (*φ*) of the thermionic emitter is high, compounds are more efficiently ionized by SI according to the Saha-Langmuir equation.[11] Oxidizing the tungsten ribbon increases its work function from approximately 4.6 eV to 6.5 eV. Neither the molecular ion M^+ nor the deprotonated ion $[M\text{-}H]^+$ was detected, likely due to their ionization energy. Imidacloprid ions that were not detected with the oxidized thermoemitter were also not observed with the metallic thermoemitter. Comparative analysis shows that the ionic composition of imidacloprid was almost identical on both the oxide and metal thermoemitters, but only some differences in ion intensity were

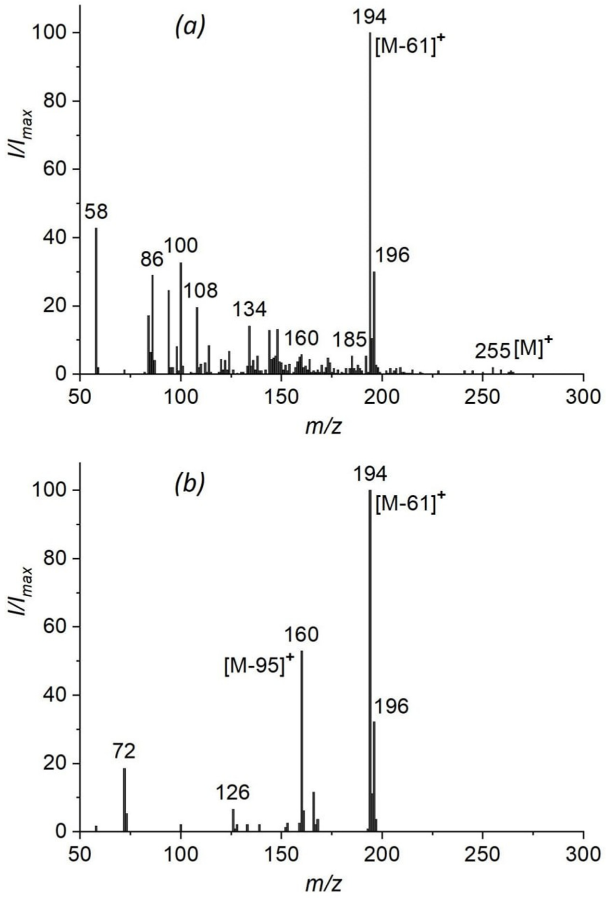

Figure 1. The SI mass spectra of imidacloprid on the surface of oxidized tungsten thermoemitter at T=1200 K (a) and the metallic tungsten thermoemitter at T=2000 K (b).

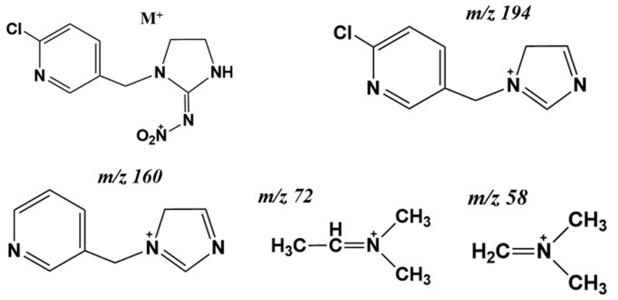

Figure 2. The structures of the ions of imidacloprid for M$^+$, *m/z* 194, *m/z* 160, *m/z* 72 and *m/z* 58.

observed on the metal tungsten thermoemitter, indicating no formation of additional ions. It can be explained by the difference in the work functions of oxidized and metallic thermoemitters. Supplementary figure 1 shows a chromatogram and mass spectrum of imidacloprid obtained by GC-MS. The electron ionization mass spectrum of imidacloprid is completely different from the SI mass spectrum. The molecular ion of imidacloprid was not detected in the mass spectrum, and the main ion at *m/z* 211 was formed by the cleavage of the NO_2 group.

Molecule adsorption occurs through the formation of a coordination bond with the adsorbent. The lone pair of electrons on the nitrogen atom is transferred to the thermoemitter, leading to the formation of a partial positive charge on the nitrogen atom. When adsorption occurs through a nitrogen heteroatom, the β bond from the nitrogen atom weakens, leading to the formation of a deprotonated ion $[M\text{-}H]^+$. Additionally, an α bond from the nitrogen atom can also form a deprotonated ion $[M\text{-}H]^+$, which may then desorb as an ion with a quadrivalent positively charged nitrogen atom.[11] Imidacloprid has two rings with four nitrogen heteroatoms, so adsorption may occur on one of these rings. According to SI regularities for amines, if adsorption involves many atoms in the molecule, the temperature threshold for the formation of the M$^+$ or $[M\text{-}H]^+$ ion shifts to a higher thermoemitter temperature.[12] However, in these experiments, such a temperature dependence was not observed for the M$^+$ ion of imidacloprid, and the $[M\text{-}H]^+$ ion was absent from the SI mass spectra. The nitrogen atom from the NO_2 group is initially charged in the imidacloprid molecule. The formation of the molecular ion M$^+$ occurs due to adsorption by the nitrogen atom in the NO_2 group, following SI rules, which is supported by the temperature dependencies of this ion (Figure 6a). The fragment ions $[M\text{-}R]^+$ form in different reaction channels. Imidacloprid adsorption occurs at one of the nitrogen heteroatoms, specifically in the N-nitroimidazole ring structure.

Figure 2 illustrates the structure of the major ions of imidacloprid, showing the heterogeneous reaction channels responsible for their formation. As seen in Figure 1a, despite the nitrogen rule, both even- and odd-mass ions (such as *m/z* 185) are present in the mass spectrum, indicating variations in the heterogeneous reaction channels determined by the adsorption centers of the molecules. In the imidacloprid molecule, these centers might be nitrogen or oxygen heteroatom. Adsorption through a nitrogen heteroatom follows the nitrogen rule, where ions with even or odd masses form depending on the number of nitrogen atoms. During adsorption, the lone pair of electrons on the nitrogen atom is drawn toward the thermoemitter, creating a partial positive charge and weakening the β bonds with the nitrogen atom. This allows the formation of radicals [M-R], which are energetically favorable to desorb as ions with a quadrivalent positively charged nitrogen atom with sp^2-hybrid orbitals. As mentioned earlier, the fragment ion at *m/z* 194 is the main ion in the imidacloprid mass spectrum. The Cl isotope line, detected at *m/z* 196 Da, easily identifies this major ion line. The ion at *m/z* 194 is formed by adsorption involving the first nitrogen heteroatom in the N-nitroimidazole structure. It is also evident in Figure 1a and 1b that the ion at *m/z* 160 lacks the Cl isotope line, which is obviously visible in the mass spectrum obtained using the metal W thermoemitter. Ions at *m/z* 144 and 126 are formed as a result of adsorption involving the nitrogen atom in the NO_2 group. In the low mass region of the mass spectrum of imidacloprid, several ions at *m/z* 108, 100, 94, 86, 84, 58 and 72 were detected, formed as a result of deep fragmentation of the molecule on the heated surface of the thermoemitter. Ions at m/z 100, 86, 84, 72 and 58 were obtained through different deep fragmentation pathways as a result of heterogeneous reactions on the adlayer.

Chlordimeform

Chlordimeform is also a nitrogen-based insecticide and is expected to be ionized more efficiently by the SI/MS method. Figure 3a shows an SI mass spectrum obtained at the oxidized thermoemitter temperature of 600 K. The spectrum consists of several ion peaks, including protonated $[M+H]^+$ ions and fragment ions $[M\text{-}R]^+$, at *m/z* values of 197, 199, 163, 159, 100, and 94. The observed ions, such as $[M\text{-}H]^+$, $[M\text{-}H\text{-}2nH]^+$, and $[M\text{-}R]^+$, were formed during the desorption of products from heterogeneous reactions, including dissociation of $(C\text{-}H)_\beta$ and $(C\text{-}C)_\beta$ bonds, dehydrogenation processes, and skeletal rearrangements of the adsorbed chlordimeform molecule. Almost all detected ions have odd *m/z* values, consistent with the nitrogen rule. The base peak was the protonated ion at *m/z* 197 in the mass spectrum. Figure 3b displays a SI mass spectrum of chlordimeform obtained at the oxidized thermoemitter temperature of 1050 K and an evaporator temperature of 385 K. It can be seen that more fragment ions were observed at higher temperatures of the thermoemitter. In addition to the protonated ion, the deprotonated ion $[M\text{-}H]^+$ with *m/z* 195 was detected. At this high temperature, the main peak in the spectrum shifts from the protonated ion to the deprotonated ion. The peak at *m/z* 197 overlaps with the Cl isotope line at

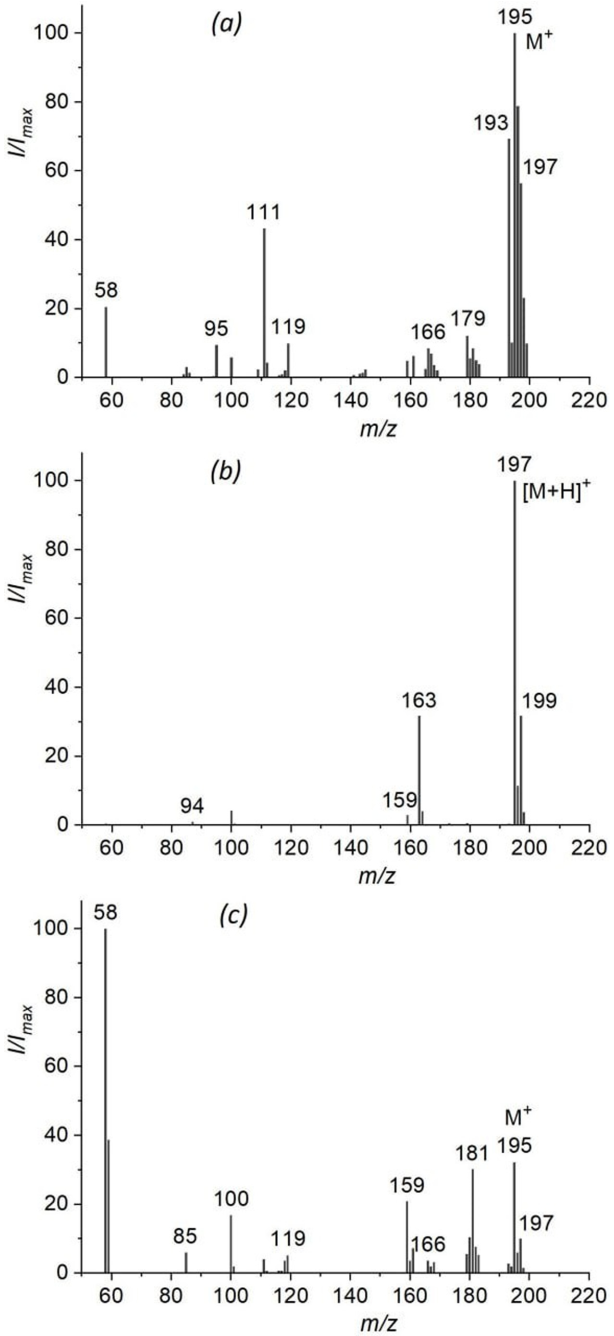

Figure 3. The SI mass spectra of chlordimeform on the surface of the oxidized tungsten thermoemitter at T=600 K (a), at T=1050 K (b) and on the metallic thermoemitter at T=2000 K.

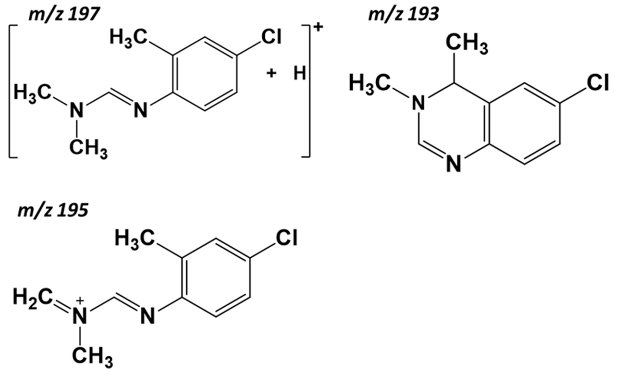

Figure 4. The structures of protonated molecular ions and deprotonated ions of chlordimeform.

m/z 195. Notably, the ion [M-H-2nH]$^+$ at *m/z* 193 also appears, indicating a structural rearrangement of chlordimeform. The structures of the protonated and deprotonated ions are shown in Figure 4. Fragment ions at *m/z* 119, 111, 100, 95, and 58 were formed through deep fragmentation on the heated surface. As with imidacloprid, the presence of the Cl atom in chlordimeform molecule makes easier the identification of ions. The formation of protonated ions is relatively unique in SI/MS for complex organic molecules due to their high ionization energies. According to established SI rules, to form protonated and molecular ions, the ionization energy of the compound must not exceed the work function of the thermoemitter by more than approximately 2 eV.[11] This process also depends on the proton acceptor and donor properties of the studied compounds.

Figure 3c shows the SI mass spectrum of chlordimeform obtained with a tungsten metal thermal emitter at 2000 K and an evaporator temperature of 385 K. The mass spectrum consists of M$^+$, [M-H-2nH]$^+$ and [M-R]$^+$ ions. Unlike imidacloprid, the mass spectrum of chlordimeform shows both molecular and deprotonated molecular ions, indicating its lower ionization energy compared to imidacloprid. The major ion was [M-R]$^+$ at m/z 58, which was formed by deep fragmentation of the molecule on the heated surface. Its structure is shown in Figure 2.

Supplementary Figure 2 presents a chromatogram and mass spectrum of chlordimeform obtained by GC-MS. It can be seen that EI mass spectrum is busier than the SI mass spectrum obtained for chlordimeform. Severe fragmentation of chlordimeform was detected by EI. The molecular ion M$^+$ was the main ion in the EI mass spectrum.

One advantage of using a static magnetic mass spectrometer in SI experiments is the ability to detect unimolecular decays of the compound. These ions provide two key characteristics of the compound. Temperature dependencies of the ratio of fragment ion currents to parent ion currents allow for the determination of the activation energy of decays (ε^*) over a specific movement time.[11,12] Using ε^* values and the statistical theory of mass spectra, one can determine the true activation energy of decays or, in the case of direct decays, the bond dissociation energy. Additionally, the molecular weight of an unknown compound can be determined using these decay ions. In contrast to imidacloprid, unimolecular decays were detected in the mass spectrum of chlordimeform. The vibrational energy accumulated by a molecule can be estimated as $E=(3N-6)kT$, where N is the number of atoms, k is the Boltzmann constant, and T is the temperature.[22,23] For chlordimeform at 1050 K, this value was estimated to be 6.61 eV. Each decay of a parent ion corresponds to two ion lines in the mass spectrum: m - a fragmentation line with tails toward lower masses and integer mass values, and m* - a diffuse fragmentation line with fractional mass values. In the chlordimeform mass spectrum, monomolecular decays of

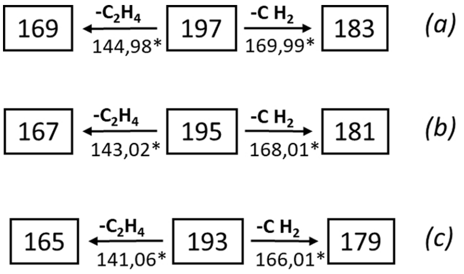

Figure 5. Scheme of monomolecular decays for $[M+H]^+$, $[M-H]^+$, and $[M-3H]^+$ ions of chlordimeform.

$[M+H]^+$, $[M-H]^+$, and $[M-3H]^+$ ions were observed. Figure 5a shows the decay scheme of the protonated $[M+H]^+$ ion at m/z 197. It can be seen that the decays occurred in two channels, resulting ions at *m/z* 183 and *m/z* 169, as well as the corresponding diffuse lines at *m/z* 169.99* and m/z 144.98*. Similarly, the decay schemes of the deprotonated $[M-H]^+$ and $[M-3H]^+$ ions are shown in Figures 5b and 5c, respectively.

The thermoemitter temperature as a function of ion currents is one of the main characteristics of the analysis of substances in the SI method. Figures 6a and 6b show the thermoemitter temperature as a function of ion currents for the main ions of imidacloprid obtained with oxidized and metallic thermoemitters, respectively. It can be observed that the dependence of imidacloprid follows a case of hard ionization, where $e(V-\varphi) >> kT$.[12] When the ionization energy of substances is higher than the work function of the thermoemitter, hard ionization occurs, i.e., only a small portion of adsorbed molecules will be ionized. The bell-shaped curves for ions at m/z 255, 148, and 100 represented reaction products indicating the simultaneous occurrence of competing processes. For example, there might be an increase in ionization of particles with increasing tempera-

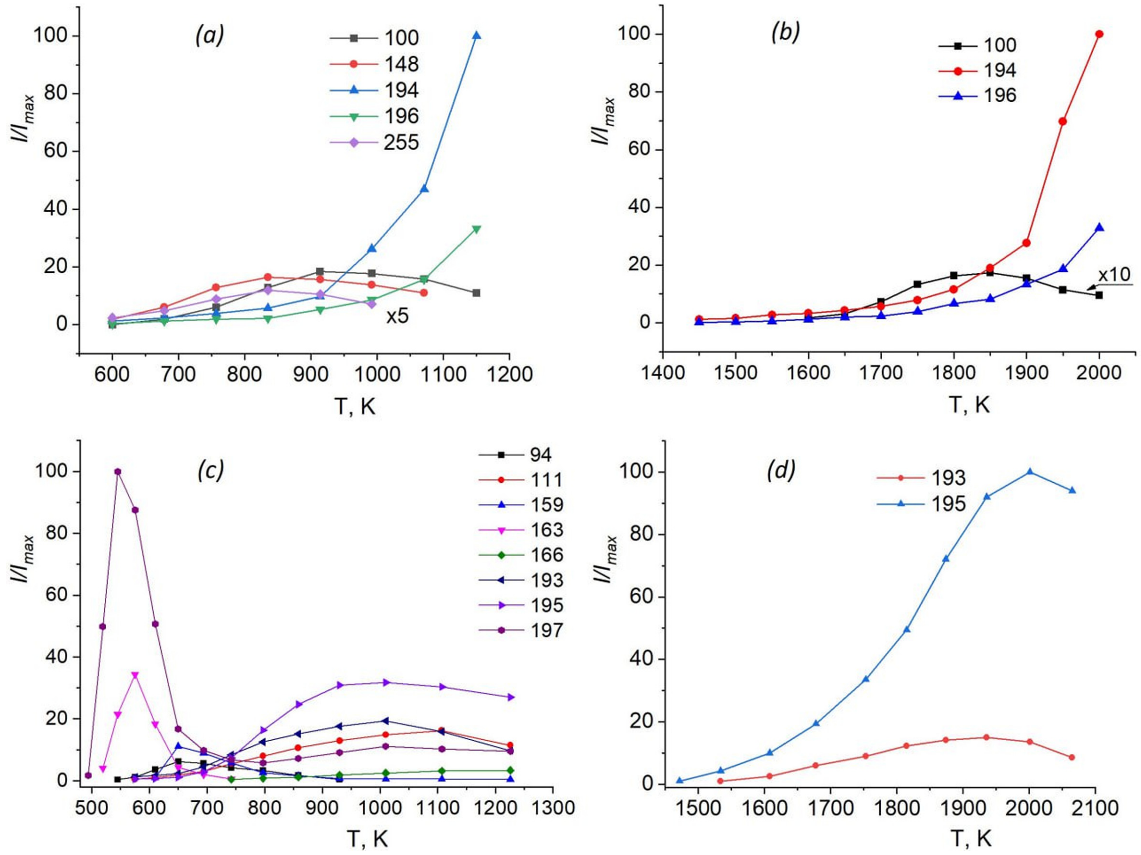

Figure 6. The dependencies of ion signals of imidacloprid and chlordimeform upon thermoemitter temperatures: (a) and (c) for oxidized thermoemitters, (b) and (d) for metallic thermoemitters. The ion signal at *m/z* 255 is magnified fivefold (a) and *m/z* 192 are magnified tenfold (b).

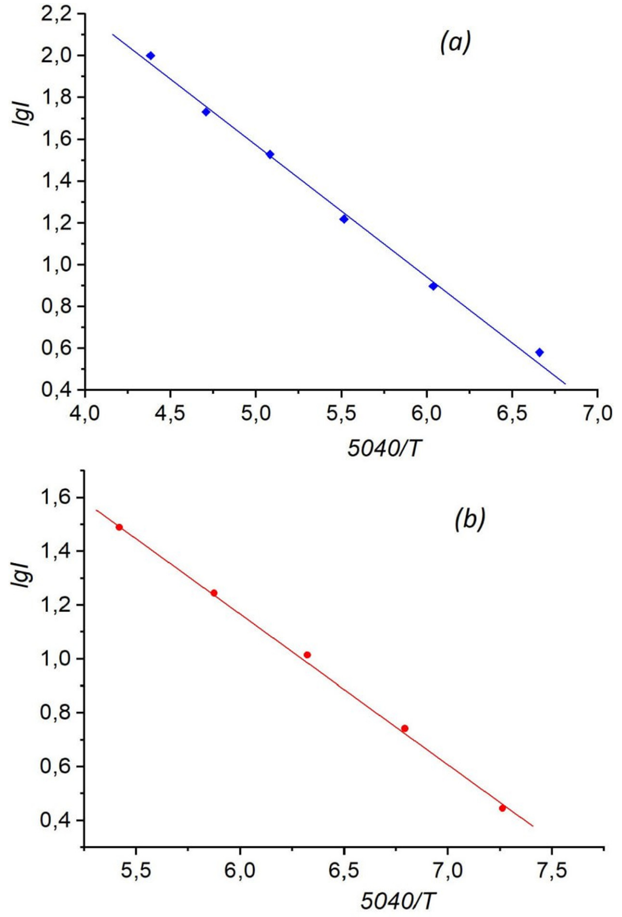

Figure 7. The Arrhenius curves for the major ion at *m/z* 194 of imidacloprid (a) and for the molecular ion at *m/z* 195 of chlordimeform (b) for determining of the ionization energy.

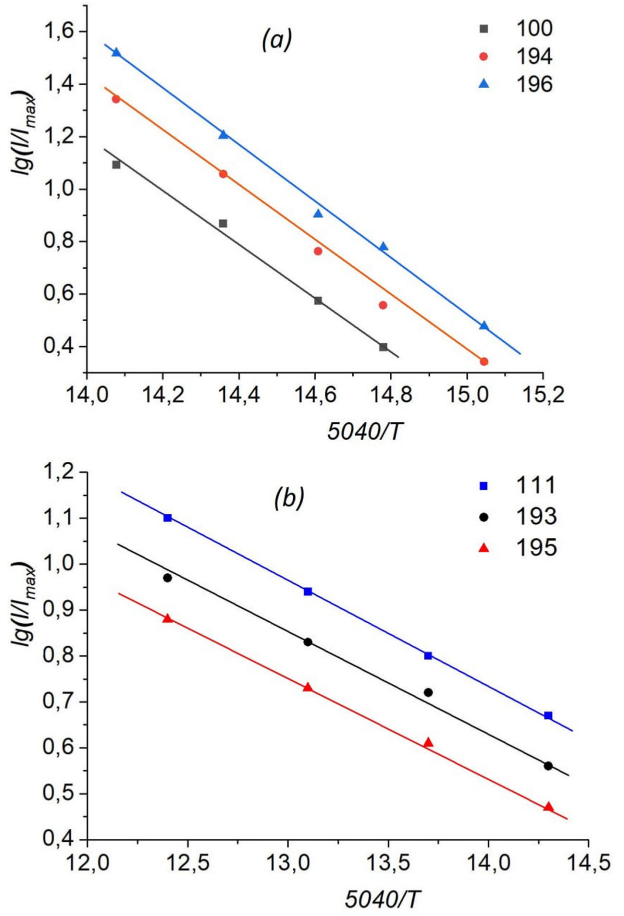

Figure 8. The Arrhenius curves for determining the heats of sublimation of imidacloprid (a) and chlordimeform (b). Data were obtained using an oxidized thermoemitter.

ture, but a decrease in the number of ionizing particles due to an increase in dissociative processes. Increasing thermoemitter temperature leads to an increase in ion current for ions of $[M-R]^+$ at *m/z* 194 and 196 (Figure 6a, 6b). Figures 6c and 6d show the thermoemitter temperature as a function of ion currents for the main ions of chlordimeform obtained in the oxidized and metallic thermoemitters, respectively. The maximum intensity of M^+ ion was detected at a low temperature of the thermoemitter, which was typical for the SI method. Interestingly, the maximum intensity of the $[M-R]^+$ ion at *m/z* 163 was also detected at 565 K, which is not typical for the SI method. Usually, the maxima of the $[M-R]^+$ ions are observed at high thermal emitter temperatures. This ion completely disappeared at 750 K, indicating its energetic instability. These curves demonstrate that the dependence of ion currents on temperature is due to the dependence of the SI coefficient on temperature, as well as the temperature dependence of the yield of chemical reactions in the adlayer, which determines the concentration of ionized particles.

To our knowledge, the ionization energies of imidacloprid and chlordimeform have not been previously determined. One of the unique features of SI its ability to estimate ionization energies using temperature-dependent ion current data. The Arrhenius plot for the major ion of imidacloprid (*m/z* 194) is shown in Figure 7a, where its ionization energy is calculated to be 7.73 eV. Figure 7b shows a similar plot for the molecular ion of chlordimeform (*m/z* 195) with a calculated ionization energy of 8.1 eV. This value is reasonable for the formation of molecular and protonated ions of chlordimeform.

Organic compounds may undergo transformation into other compounds of the same molecular weight and similar structure due to the thermal effect in the evaporator before evaporation. To confirm whether the observed ions were formed from the parent molecules, Arrhenius plots of ion current versus evaporator temperature were plotted for both compounds (Figures 8a and 8b). The same slope of these curves confirmed that the detected ions were derived from the parent molecules.[27] Furthermore, the heats of sublimation for imidacloprid and chlordimeform were calculated to be 0.68 eV and 0.62 eV, respectively.

Conclusions

Imidacloprid and chlordimeform molecules were studied on oxidized and metallic thermoemitters in electric fields $E<10^5$ V/cm using the SI/MS method. In the case of imidacloprid, both mass spectra consisted of $[M-R]^+$ ion lines; however, the radical cation M^+ of imidacloprid was detected only on the oxidized tungsten thermoemitter. This difference can be explained by the different work functions of the metallic and oxidized thermoemitters. The ionization energy of the formed ions is significantly lower than that of the imidacloprid molecule. Almost all of the formed ions of imidacloprid have an even number of electrons and can be represented as ions with quadrivalent positively charged nitrogen atoms. For chlordimeform, protonated ion $[M+H]^+$, M^+, $[M-H]^+$, $[M-H-2nH]^+$, and $[M-R]^+$ were detected in the mass spectrum on the oxidized surface. However, the protonated ion of chlordimeform was not detected on the metallic thermoemitter. Both compounds were efficiently ionized on the oxidized tungsten thermoemitter. However, the ion currents of the formed ions on the metal thermoemitter were approximately two orders of magnitude lower than those of the oxidized ones. The obtained EI mass spectra for both compounds were much more complex than the SI mass spectra.

The determined ionization energy of the major ion at *m/z* 194 for imidacloprid was 7.73 eV, while it was 8.15 eV for the M^+ ion of chlordimeform. In contrast to imidacloprid, unimolecular decays were observed in the mass spectra of chlordimeform, which provides two key characteristics of the compounds. The heats of sublimation of imidacloprid and chlordimeform were determined from Arrhenius plots to be 0.68 eV and 0.61 eV, respectively. The major ions obtained from these analytes could serve as indicator lines in real-world samples of imidacloprid and chlordimeform, as previously found in other organic compounds.

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The research does not contain the conflict of interest.

Notes

†Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: xx.xxxx/xxxxx/

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