Russian Chemical Reviews

September 1982

Translated from *Uspekhi Khimii*, 51 1425-1446 (1982)

U.D.C. 537.58:547.9+543.51+543.54+543.8

Surface Ionisation of Organic Compounds

E.Ya.Zandberg and U.Kh.Rasulev

The equilibrium thermal emission of positive ions of organic compounds from the surfaces of heated solids is examined. The possibilities of employing this phenomenon in the physical and analytical chemistry of organic compounds are illustrated.
The bibliography includes 75 references.

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I. INTRODUCTION

Surface ionisation (SI) consists of the formation of ions in the course of the thermal desorption of species from the surface of a solid. In the general case surface ionisation includes three consecutive stages: the arrival of the species on the surface; the establishment of thermal and charge equilibria between the adsorbed species and the solid; evaporation of the species from the surface of the solid. In the last stage the single solid–species system breaks up into two subsystems over distances from the solid (x_{cr}) of the order of magnitude of atomic dimensions and the final charge state of the desorbed species is established. It depends on the probability of the isoenergetic electron exchange between the species and the solid. In a simplified form, this is illustrated in Fig.1: the species can become a positive ion if its valence electron can occupy a vacant level in the solid; conversely, if the electron of the solid can pass to a vacant orbital of the species, the latter can be desorbed in the form of a negative ion.

Surface ionisation was discovered by Langmuir and Kingdon in 1923:[1] a current comprising positive ions passed through a vacuum diode with an incandescent tungsten wire when caesium vapour was admitted. Langmuir and Kingdon obtained an expression for the degree of surface ionisation of atoms α within a closed uniform metallic cavity at a temperature T (Kingdon and Langmuir[2]) (the Saha–Langmuir formula):

$$\alpha = A \exp[e(\varphi - V)/kT], \quad (1)$$

where $\alpha = n^+/n^0$ is the ratio of the equilibrium concentrations of the ions and atoms within the cavity, A the ratio of

the statistical weights of the ionic and neutral states of the atoms ($A = 1/2$ in the case of Cs), $e\phi$ the electron work function of the wall of the cavity, V the ionisation potential of caesium, k the Boltzmann constant, and e the electronic charge.

It was established in subsequent years that positive atomic ions of the majority of elements and the negative ions of many elements can be obtained by surface ionisation. Ion sources for different purposes and detectors of atomic fluxes have been devised on the basis of surface ionisation. A general theory of the phenomenon has been developed. It describes the formation of positive and negative ions on ionisation of the atoms of any elements, not only within closed cavities but also on open surfaces which are both uniform and non-uniform as regards emission; the influence on α of external electric fields, which accelerate ions, has been examined.

The most complete theory of the phenomenon is described in a monograph[3]. It is based on the ideas of statistical thermodynamics and leads to explicit expressions for the current densities in different cases of ionisation. The possibility of the experimental determination of the parameters in these expressions from the measured current has become the basis of the development of a new application of surface ionisation—its employment as a method for the physicochemical investigation of many properties of solids, ionisable atoms, and the characteristics of the interaction of atoms with a solid.

More than twenty such methods have been developed recently, in particular, those for the determination of ionisation potentials, electron affinities, the lifetimes of atoms and ions on the surface, the heats of desorption of atoms and ions, and the emission characteristics of solids, for the study of phase transitions in adsorbed layers, for the determination of the activities of catalysts in heterogeneous dissociation reactions, etc.[3-5]. Evidently the surface ionisation of molecules, radicals, and complexes can yield valuable information about the properties of these species and also about their interaction with a solid.

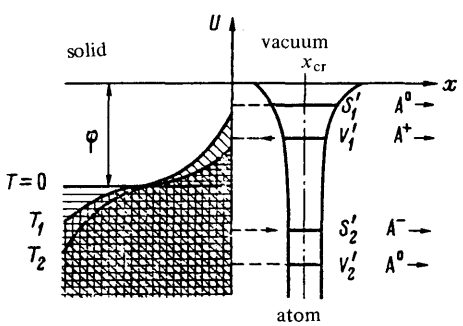


Figure 1. Illustration of the charge state of the desorbed species; $T < T_1 < T_2$.

Experimental studies on the surface ionisation of organic compounds (polyatomic species) have been begun recently. The possibility of the thermal desorption of organic ions was first indicated in studies carried out towards the end of the 1950's and the beginning of the 1960's;[6-10] some of these yielded elaborate mass spectra of the ions obtained on ionisation of the residual gases and vapours in the mass spectrometer[8-10], which can be accounted for only by the ionisation of organic compounds, for example, the vapours of the oils seeping from the pumps. Next, a change in the conductivity of flow-type diodes with an incandescent platinum or a molybdenum anode when specific organic compounds (the vapours of hydrocarbons, alcohols, ethers, and ketones) mixed with air or oxygen at atmospheric pressure were passed through them was observed[11-14]; however, it was not possible to observe the ionisation of the same compounds with the aid of the mass-spectrometric technique[10].

A number of studies on the surface ionisation of organic compounds involving the formation of negative ions have been performed by Page and coworkers using a magnetron technique. A systematic account of these studies has been published[15]; the electron affinities of many molecules and radicals have been determined with the aid of surface ionisation. However, subsequent mass-spectrometric studies established that the composition of the negative ions put forward in Page's studies did not correspond to reality[16,17] and that the ions were most probably formed not by surface ionisation but via some other mechanisms in secondary and tertiary side reactions associated with the emission of thermal electrons from the emitter[17]. Thus certain electron affinities are incorrect and it is regrettable that they are still quoted in the reference literature (for example, by Kondrat'ev[18]).

Systematic studies on the surface ionisation of organic compounds were begun in 1965 at the Ioffe Physicotechnical Institute of the USSR Academy of Sciences. Initially their aim was to discover the classes of organic compounds capable of ionising on heated surfaces. In the course of these studies it was found that, apart from the equilibrium thermal ionisation, non-equilibrium thermal ionisation also occurs, for example, in those cases where the energy evolved on decomposition of the molecule on the surface participates in the ionisation of the fragments[19-21]. Certain organic peroxides ionise in this way; the SI emission relations cannot be used to describe the ionisation of this type. As regards surface ionisation with formation of negative ions, hitherto it has been possible to obtain only the ions of small molecular fragments as a consequence of the small (as a rule) electron affinities of organic molecules and radicals and the requirement that the emitters of ions have high temperatures[17].

Extensive data have already accumulated on the surface ionisation of individual organic compounds with formation of polyatomic positive ions; the classes of ionisable compounds have been found, the principal rules governing the phenomenon have been established, and a number of its applications have been developed. These problems are considered in the present review.

II. CHARACTERISTICS OF THE SURFACE IONISATION OF ORGANIC COMPOUNDS

The theory of surface ionisation does not impose limitations on the composition of the ionising species. These can be polyatomic species, which includes both species incident on the surface and species formed from them as a result of chemical reactions in the adsorbed layer. The only important factor is that thermal and charge equilibria are established on the surface during the lifetime of the species.

If the molecule on the surface of the emitter can be converted into i types of new species, the incident flux of molecules ν can be conveniently represented as one

comprising i effective fluxes ν_i, each of which forms species of only one kind. There is then a relation between ν_i and ν:[22]

$$\nu_i(T, E) = \gamma_i(T, E)\nu, \quad (2)$$

where $\gamma_i(T, E)$ is a coefficient, which depends, for a given molecule–emitter pair, on the emitter temperature T and the electric field strength E at its surface. It defines the concentration of the ith species in the adsorbed layer as a result of all the processes occuring in it[23]. The ionisation of each kind of species can be treated independently of the ionisation of species of another type.

When the ion current is generated on the surface, the ratio of the charged component of the evaporating flux to its uncharged component $\alpha_i = \nu_i^+/\nu_i^0$ is given by the following formula for a surface uniform with respect to the electron work function ϕ in weak electric fields:

$$\alpha_i = A_i \exp\{e[(\varphi - V_i) + (eE)^{1/2}]/kT\}. \quad (3)$$

For polyatomic ith species, V_i is the first adiabatic ionisation potential and $A_i = Q_i^+/Q_i^0$ is the ratio of the total partition functions (translational, rotational, vibrational, nuclear, and electronic) for the charged and neutral species at the temperature T.[20] By definition, $0 < \alpha_i \leq \infty$.

As in the ionisation of atoms, a convenient characteristic is the ionisation coefficient

$$\beta_i = \nu_i^+/\nu_i, \quad (4)$$

which by definition lies in the range $0 \leq \beta_i \leq 1$.

Under steady-state conditions (when the effective flux ν_i is equal to the evaporating flux, i.e. $\nu_i = \nu_i^+ + \nu_i^0$), α_i and β_i are linked by the relation

$$\beta_i = (1 + 1/\alpha_i)^{-1}. \quad (5)$$

The current due to ions of the ith type is

$$I_i = e\nu_i^+ F = e\nu_i\beta_i F = e\nu\gamma_i\beta_i F, \quad (6)$$

where F is the area of the emitting surface. We obtain from Eqns.(3), (5), and (6)

$$I_i = e\nu\gamma_i F \Big/ \left\{1 + \frac{1}{A_i}\exp\left[\frac{e}{kT}(V_i - \varphi - (eE)^{1/2})\right]\right\}, \quad (7)$$

In two cases common in practice Eqn.(7) simplies significantly.

1. The case of difficult ionisation: $e[V_i - \phi - (eE)^{1/2}] \gg kT$. Only a small proportion of the incident species are ionised under these conditions; we obtain from Eqn.(7)

$$I_i \simeq e\nu\gamma_i F A_i \exp\left[\frac{e}{kT}(\varphi + (eE)^{1/2} - V_i)\right]. \quad (8)$$

The relation between I_i and T may be exponential or more complex owing to the relation between γ_i and T.

2. The case of easy ionisation: $e[\phi + (eE)^{1/2} - V_i] \gg kT$. We then obtain from Eqn.(7)

$$I_i(T, E) \simeq e\nu\gamma_i F, \quad (9)$$

i.e. virtually every species produced on the surface ionises.

If the emitter is non-uniform with respect to ϕ (for example, is polycrystalline), then, when the contact potentials of the spots on its surface are compensated by the external electric field (electric field strengths in the range $E \approx 10^3$–10^4 V cm^{-1} are usually sufficient for this), the ionic current is equal to the sum of the currents from the individual spots. In this case the ionisation within narrow temperature ranges can be represented as occurring on a uniform surface; it is characterised by the effective parameters ϕ^*, A_i^* (Zandberg and Ionov[3]), and γ_i^*. The form of Eqns.(7)–(9) then remains unaltered.

III. EXPERIMENTAL TECHNIQUE

The methods used to investigate the surface ionisation of organic compounds must ensure the following conditions: (1) reliable identification of the ions; (2) the possibility of elucidating the problem of the thermal equilibrium in the adsorbed layer of the species; (3) the application of ion emitters with a high work function (the values of V for organic compounds exceed 7–8 eV [18]), which is stable in time; (4) the possibility of measuring T and ϕ under working conditions.

Special high-vacuum mass-spectrometric devices have been constructed at the Ioffe Physicotechnical Institute for the investigation of the surface ionisation of organic compounds[19,20,24]. The ionic currents due to the thermal ionisation of the vapours of the residual substances are virtually absent in these devices. Vacuum distillation of the substances introduced is used and the surface ionisation and electron ionisation mass spectra are compared at different stages of the distillation process (for this purpose, there is an additional source of ions with electron ionisation). If the sample contains impurities, it is possible to establish by this procedure to which substances the ions obtained refer and this is important in view of the selectivity of the surface ionisation with respect to V: a small amount of impurity with a smaller value of V can mask the current due to the main substance [for example, for two substances with $V_1 > V_2 > \phi$ and $V_1 - V_2 = 2eV$, we obtain from Eqn.(8) $I_2/I_1 \approx 10^9$ at 1000 K].

The problem of the thermal equilibrium is studied by analysing the energies of the ions on the basis of the normal components of the initial translational velocities[3]. In principle, such analogy is insufficient in the case of polyatomic species, since all types of internal motion in the latter must also correspond to equilibrium. However, one can assume that in the adsorbed layers of the species there is the same sequence in the attainment of equilibrium by different forms of motion as in the gas phase, i.e. that the vibrational processes are slowest[25]. The thermal equilibrium in the translational motion of species indicates equilibrium in their vibrational motion. Since the energy of the bond between the chemisorbed molecules and the solid is of the same order of magnitude as the energy of the bonds between the atoms in the molecule, the equilibrium distribution of ions with respect to kinetic energy may indicate also the attainment of equilibrium with respect to all types of motion of the adsorbed species.

The search for the most effective emitters in order to obtain the ions of organic compounds led to oxidised metals exhibiting a catalytic activity in relation to the dissociation of the molecules and higher values of ϕ.[8,26,27]. Under the influence of organic compounds, the emission properties of oxidised metals vary with time[27], so that, in order to increase their continuous operation time, the vapours of the test substances are admitted only until the attainment of a pressure of approximately 1×10^{-5}–1×10^{-4} Pa. In view of the non-uniformity of the oxidised metals with respect to ϕ,[26,28] provision is made for the measurement under working conditions of both the effective electron work function ϕ_e^* and the effective ion work function ϕ_i^*. A Knudsen cell with a substance difficult to ionise, for example, bismuth ($V = 7.287$ eV) is present in the surface-ionisation ion source in order to measure ϕ_i^*.

At the surface of the emitter the strength of the external electric field $E \approx 10^3$–10^5 V cm^{-1}, this is sufficient to compensate for the contact fields of the spots but is much smaller than required for the desorption of the ions by the field[29].

The search for substances capable of surface ionisation has been carried out among compounds of different classes. Simple hydrocarbons, alcohols, ethers, ketones, nitrocompounds, and nitriles do not ionise[19,30]. Amines, hydrazines and their various derivatives, phosphines, arsines, and certain oxygen-containing substances (phenols, organic acids, and benzene derivatives) do ionise. Compounds containing Group VA elements, which form polyatomic radicals containing these heteroatoms, ionise with the greatest efficiency.

IV. CHARACTERISTIC FEATURES OF THE FORMATION OF IONS BY ORGANIC COMPOUNDS CONTAINING GROUP VA HETEROATOMS

The surface ionisation of approximately 70 compounds of different classes[30] (mainly the effectively ionisable amines[30–35], hydrazines[36], and their derivatives[34,37,38]) has now been investigated, mainly on emitters consisting of oxidised tungsten[26] and also on tungsten, molybdenum, nickel, rhenium, and iridium, oxidised molybdenum and nickel, and nichrome emitters[27,28,30].

In all cases the initial kinetic energy of translation of the ions desorbed from the surface of the emitter corresponded to equilibrium with the temperature of the emitter[24,31]. The currents due to molecular ions and the ions derived from the dissociation products of the molecules on the surface of the emitter depended linearly on the vapour pressure of the test substance, while the currents due to the associated species $(M + H)^+$, obtained on ionisation of primary and secondary amines and phosphines, depended on the square of the vapour pressure[39].

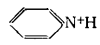
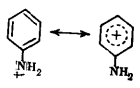
In virtually all publications the surface ionisation mass spectra are presented in the form of tables such as Table 1, where the following parameters are indicated in addition to the mass number m: the maximum ionic current density j (A cm^{-2}) referred to the vapour pressure $p = 1.33 \times 10^{-5}$ Pa, measured with an ionisation gauge calibrated against nitrogen†, the corresponding emitter temperatures, the postulated chemical structures of the ions (for this purpose, the surface ionisation of labelled compounds has been studied in a number of instances[35,36]), and the ionisation potentials of the ionising species estimated by SI methods.

In the ionisation of *alkylamines*[30–33] (the SI mass spectra of which are presented in Table 1), the following features were discovered.

1. The products of the chemical reactions of the molecules of the initial amines (mainly dissociation reactions) ionise on the surface of the emitter and not the molecules of the initial amines themselves.

2. In the SI mass spectra the number of lines is small. They may contain, regardless of the material of the emitter, lines due to ions within the set $(M - H)^+$, $(M - Alk)^+$,

Table 1. The surface-ionisation mass spectra of a series of amines.

Compound	M, a.u.	V_M, V	m_i, a.u.	Ion	j, A cm^{-2}	T, K	Postulated structure of ion	V_i, V	Refs.
Ethylamine	45	8.87 [40]	46	$(M+H)^+$	$3\cdot10^{-14}$	600	$C_2H_5N^+H_3$	$\lesssim$7.8	[32]
			44	$(M-H)^+$	$1\cdot10^{-12}$	1100	$CH_3-CH=N^+H_2$	$\lesssim$8.3	
Diethylamine	73	8.01 [40]	74	$(M+H)^+$	$1\cdot10^{-9}$	550	$(C_2H_5)_2N^+H_2$	$\lesssim$7.2	[32]
			72	$(M-H)^+$	$3\cdot10^{-8}$	700	$CH_3-CH=N^+H-C_2H_5$	$\lesssim$7.2	
			70	$(M-3H)^+$	$1\cdot10^{-9}$	700	$CH_3-CH=N^+H-CH=CH_2$	$\lesssim$7.4	
			58	$(M-CH_3)^+$	$2\cdot10^{-10}$	1100	$CH_2=N^+H-C_2H_5$	$\lesssim$7.8	
Triethylamine	101	7.50 [40]	102	$(M+H)^+$	traces	550	$(C_2H_5)_3N^+H$	—	[32]
			100	$(M-H)^+$	$4\cdot10^{-7}$	600	$(C_2H_5)_2N^+=CH-CH_3$	$\lesssim$6.9	
			98	$(M-3H)^+$	$2\cdot10^{-9}$	600	$C_2H_3(C_2H_5)N^+=CH-CH_3$	—	
			86	$(M-CH_3)^+$	$2.5\cdot10^{-7}$	1150	$(C_2H_5)_2N^+=CH_2$	$\lesssim$7.1	
			84	$(M-CH_3-2H)^+$	$2\cdot10^{-9}$	1150	$C_2H_3(C_2H_5)N^+=CH_2$	—	
n-Pentylamine	87	—	88	$(M+H)^+$	$3.5\cdot10^{-11}$	650	$CH_3(CH_2)_4N^+H_3$	$\lesssim$7.7	[31]
			86	$(M-H)^+$	$7\cdot10^{-10}$	1200	$CH_3(CH_2)_3CH=N^+H_2$	$\lesssim$8.0	
			85	$(M-2H)^+$	$1.5\cdot10^{-11}$	1200	$C_5H_{11}N^+$	—	
			84	$(M-3H)^+$	$2\cdot10^{-10}$	1200	$CH_3-CH_2-CH=CH-CH=N^+H_2$	—	
			83	$(M-4H)^+$	$7\cdot10^{-13}$	1200	$C_5H_9N^+$	—	
			82	$(M-5H)^+$	$7\cdot10^{-12}$	1200	$CH_2=CH-CH=CH-CH=N^+H_2$	—	
			81	$(M-6H)^+$	$7\cdot10^{-13}$	1200	$C_5H_7N^+$	—	
			80	$(M-7H)^+$	$7\cdot10^{-12}$	1200	$C_5H_5N^+H$	—	
Pyridine	79	9.32 [40]	80	$(M+H)^+$	$3\cdot10^{-13}$	550		$\lesssim$7.5	[31]
Aniline	93	7.69 [41]	93	M^+	$3\cdot10^{-11}$	1100		7.65+0.07	[42]

Notation. M is the molecular weight of the substance, V_M its ionisation potential, m_i the mass of the ion, and j the current density.

†In this calibration of the gauge, there is an error in the determination of the vapour pressure p of organic substances resulting in an overestimate. Therefore the values of j presented are correspondingly too low.

$(M + H)^+$, $(M - H - nH)^+$, and $(M - Alk - nH)^+$.

3. As a rule, all the ions formed in the surface ionisation of alkylamines have an even number of electrons and they can be represented as ions containing quadrivalent positively-charged nitrogen atoms with sp^3-, sp^2-, or sp-hybrid orbitals. The current density due to such ions greatly exceeds that of radical-ions.

4. The ionisation potentials of the radicals (M - H) and (M - Alk), as well as the associated species (M + H) are as a rule lower than the V_M for the initial molecules. Therefore if the ions M^+ are in fact formed via surface ionisation under the conditions of the experiment, they cannot be detected against the background of a significantly more intense line due to the isotopic ions of the $m + 1$ radicals (M - H).

5. The current densities of isotypical radical and associated species depend on the nature of the groups attached to the nitrogen atom: the current density increases significantly as the hydrogen atoms in the amino-group are substituted by alkyl groups.

6. The efficiency of the surface ionisation of alkylamines, particularly secondary and tertiary amines, is high. Thus the overall ion current density in the ionisation of tertiary alkylamines on oxidised tungsten reaches approximately 0.1 A Pa^{-1} cm^{-2}, i.e. each 2–5 molecules of the amine arriving on the surface of the emitter lead to the formation of one ion on average.

7. The temperature variations of the ion currents of each species are characteristic (Fig.2), which is due to the difference between the temperature variations of the yields of the reaction involving the formation of ionisable species of each kind; reactions leading to the formation of associated species proceed at lower temperatures than the dissociation reactions; the temperature threshold of the reaction resulting in the formation of the (M - Alk) species is much higher than for the reaction in which the hydrogen atom is abstracted; the threshold ionisation temperatures for the (M + H) and (M - H) species are determined by the threshold surface ionisation temperature[30,39] and those for the (M - Alk) species are determined by the temperature threshold of the reaction[23,30].

8. The species (M + H) are formed on the surface of the emitter as a result of the association of the adsorbed molecules via hydrogen bonding and of the subsequent decomposition of the associated species[39].

The influence of substituents in the molecules of amines on the composition of their SI mass spectra and on the ionisation efficiency has been demonstrated for the SI of trimethylamines of the type $(CH_3)_2N-CH_2-R$, where $R = CH_3$ (I), $CH = CH_2$ (II), $N(CH_3)_2$ (III), CN (IV), C_6H_5 (V), or p-$C_6H_4NO_2$ (VI).[34,35] The SI mass spectra of these substances consist of lines due to the ions $(M - H)^+$ and $(M - R)^+$. The efficiency of the formation of the ions $(M - H)^+$ depends significantly on the electronegativity of the substituent R: the current densities of the ions $(M - H)^+$ vary over five orders of magnitude (from approximately 2×10^{-2} to approximately 2×10^{-7} A Pa^{-1} cm^{-2}) and are qualitatively correlated with the Taft substituent constants.

The radicals (M - R) derived from the above trimethylamines are identical, namely $(CH_3)_2N\dot{C}H_2$; on surface ionisation, they give rise to the stable ions $(CH_3)_2N^+CH_2 \rightleftharpoons (CH_3)_2NC^+H_2$, stabilised by the presence of an unshared electron pair at the nitrogen atom and the electron-donating methyl groups. However, the current densities of the ions derived from these radicals and the form of the relations between j and T for ionisation on the same emitter differ appreciably (Fig.3). This is associated with the difference between the $\gamma-T$ relations. The current density of the ions $(M - R)^+$ produced by tetramethyldiaminomethane ($j \gtrsim 5 \times 10^{-2}$ A Pa^{-1} cm^{-2}) and the absence of a dependence of j on T over a wide temperature range lead to the conclusion that the ionisation potential of this radical $V < \phi_i^*$. Here $\beta \cong 1$ (Zandberg and Ionov[3]) and it follows from Eqn.(9) that the $I-T$ relations in all the remaining cases reproduce the $\gamma-T$ relations, while the ratios of the values of j are the same as the ratios of the γ.

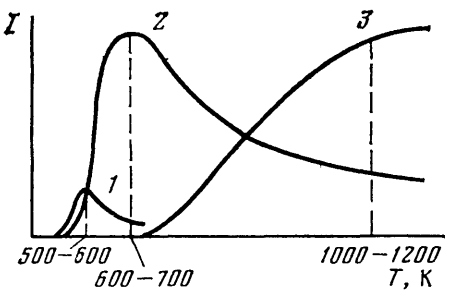


Figure 2. Temperature variation of the currents in the surface ionisation of alkylamines on oxidised tungsten[43]: *1*) $(M + H)^+$ ions; *2*) $(M - H)^+$ ions; *3*) $(M - R)^+$ ions.

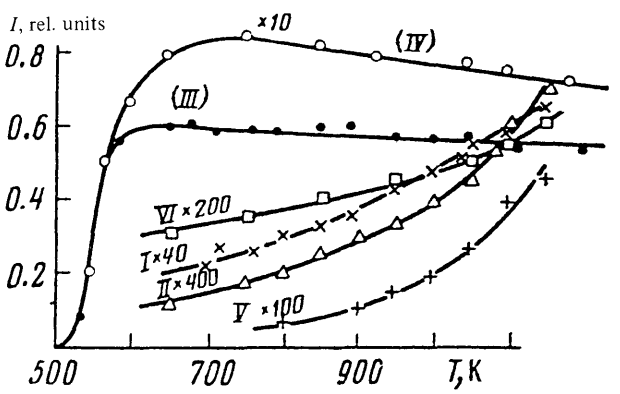


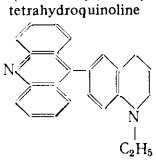
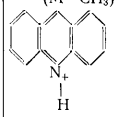
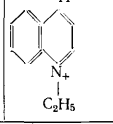
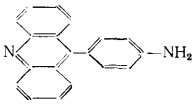
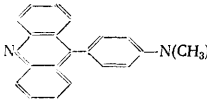
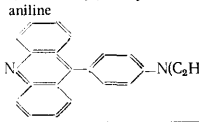
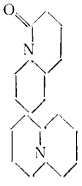
Figure 3. Temperature variation of the currents due to the $(M - R)^+$ ions in the ionisation of the substituted trimethylamines (I)–(VI).[34]

A qualitative correlation between the yield on the emitter of the products of the reactions involving the formation of the radicals (M - R) and the energy of formation of the radical R can be traced. The lower the latter, the higher the current density due to the ions $(M - R)^+$. It is noteworthy that the overall density of the currents due to all the ions in the surface ionisation of substituted trimethylamines is high and changes only slightly on passing from one compound to another. Thus the overall current density is in the range ~10^{-2}–10^{-1} A Pa^{-1} cm^{-2} for compounds (I)–(V).[34]

The ionisation of more complex bases such as acridinyltetrahydroquinolines and acridinylanilines with different substituents at the nitrogen atom, benzimidazoles, the alkaloid allomatrine, etc. (the SI mass spectra of some of these represented in Table 2) obeys the same rules governing

the formation of ions as in the surface ionisation of simple amines[37]; in particular their mass spectra consist of the same characteristic set of lines due to the ions $(M + H)^+$, M^+, $(M - H)^+$, $(M - R)^+$, and $(M - H - 2nH)^+$.

Table 2. The parameters of the mass spectra of certain *N,N*-heterocyclic compounds[37].

Compound	m_i, a.u.	Ion	Relative intensity, %	*T*, K	*j*, A cm-2
6-(9'-Acridinyl)-1-ethyl-1,2,3,4-tetrahydroquinoline 	339	$(M+H)^+$	0.5		—
	338	M^+	4		—
	337	$(M-H)^+$	11		—
	335	$(M-3H)^+$	100	1000	$\sim 5\cdot10^{-8}$ (90)
	323	$(M-CH_3)^+$	1.5		—
	180 		2		—
	158 		10		—
4-(9'-Acridinyl)aniline 	272	$(M+H)^+$	15		—
	271	M^+	100	1150	$2\cdot10^{-11}$ (120)
4-(9'-Acridinyl)dimethyl-aniline 	299	$(M+H)^+$	1		—
	298	M^+	2		—
	297	$(M-H)^+$	100	150	$\sim 2\cdot10^{-10}$ (120)
4-(9'-Acridinyl)diethyl-aniline 	327	$(M+H)^+$	—		—
	326	M^+	1		—
	325	$(M-H)^+$	67		—
	323	$(M-3H)^+$	33		—
	321	$(M-5H)^+$	11		—
	311	$(M-CH_3)^+$	100	1150	$1\cdot10^{-9}$ (100)
Allomatrine 	249	$(M+H)^+$	—		
	247	$(M-H)^+$	75		
	245	$(M-3H)^+$	80		
	243	$(M-5H)^+$	100	1170	$1\cdot10^{-8}$ (25)
	241	$(M-7H)^+$	60		
	239	$(M-9H)^+$	20		
	235	$(M-11H)^+$	10		
	235	$(M-13H)^+$	2		

*The evaporator temperature (°C) is given in brackets.

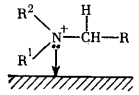
Simple rules for the formation of ions have been formulated on the basis of the analysis of the SI mass spectra of amines and their derivatives whereby one can predict the composition of the ions in the SI mass spectra of the amines and estimate the ion current densities[37,43]. These rules can be accounted for by the high selectivity of the surface ionisation in relation to the ionisation potentials *V* of the ionising species, the favourable energetic features of the formation of ions with saturated bonds, which in the case of amines can be represented by ions with a quadrivalent positively-charged nitrogen atom having hybrid orbitals, and by the dependence of *V* for the ionising species on the electronegativities of the substituents. Thus the ionisation of the amine $R^1R^2N\text{-}CH_2R$ always results in the formation of ions derived from the radicals (M - H) and (M - R), obtained on dissociation of the β-bond (relative to nitrogen) in the adsorbed molecules. The current density of the ions $(M - H)^+$ is determined by the electronegativities of the substituents R^1, R^2, and R. In the case of alkylamines, $j \cong (10^{-6}\text{–}10^{-4})$ for primary amines, $\sim 10^{-3}$ for secondary amines, and $\sim(10^{-2}\text{–}10^{-1})$ A Pa^{-1} cm^{-2} for tertiary amines[30]. The current density of the ions $(M - R)^+$ depends on the electronegativities of the substituents R^1 and R^2 and also on the energy of formation of the radical R. If R^1 and R^2 are alkyl groups, then the current density of the ions $(M - R)^+$ is $\sim(10^{-2}\text{–}10^{-1})$ A Pa^{-1} cm^{-2}.[30,32–34]

The lines due to the ions $(M - H - 2nH)^+$ and $(M - R - 2nH)^+$, which are formed on ionisation of the dehydrogenation products of the molecules on the surfaces of oxidised metals (when metallic emitters are used, these ions are hardly detected), should be observed in the SI mass spectra on ionisation of molecules with alkyl substituents. The intensity of the lines due to these ions on ionisation of amines with linear alkyl substituents is lower than the intensity of the lines of the ions $(M - H)^+$ and $(M - R)^+$ and decreases with increase of *n*. In the mass spectra of alicyclic compounds with the nitrogen atom in the ring, the intensity of the lines due to the ions $(M - H - 2nH)^+$, in which the ring has been aromatised, may be considerable and may increase the intensity of the lines due to the ions $(M - H)^+$.[37]

The lines of the ions $(M + H)^+$, formed on ionisation of the complexes (M + H), should be always present in the SI mass spectra of primary and secondary amines at low temperatures of the emitter; the complexes are obtained as a result of the self-association of the molecules on the surface of the emitter[39]. The ions $(M + H)^+$ can be detected also in the ionisation of tertiary amines; however, in this case the complex formation is due to the presence of polar molecules, for example, H_2O, in the residual gas within the mass spectrometer[32,34].

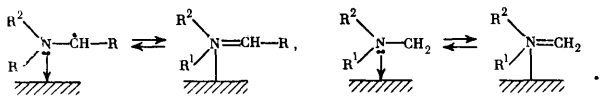
Points due to molecular ions M^+ which are susceptible to measurement can be obtained in those cases where the ionisation potentials of the molecules do not exceed the work function of the emitter by more than approximately 2 eV and during their lifetime in the adsorbed state the molecules must not be fully converted into species of another chemical composition. This happens, for example, in the case of aromatic amines and nitrogen-containing heterocyclic compounds[37,42]. However, even if the above conditions are fulfilled, the lines due to the ions M^+ can be more readily detected, as already mentioned, on ionisation of substances which do not form the ions $(M - H)^+$ effectively.

The rules governing the formation of ions, common to all the amines and their derivatives and independent of the material of the emitter, have been used to elucidate the mechanism of the adsorption of amine molecules and their reactions on the emitter[20,43]. One may conclude that the amines are adsorbed as a result of the formation of a coordinate bond with the adsorbent; the withdrawal of the electron pair to the emitter which occurs under these conditions leads to the formation of a partial positive charge on the nitrogen atom:



This causes a significant weakening of the β-bonds relative to the nitrogen atom[44] and explains the formation of the

radicals (M - H) and (M - R) on the surface of the emitter:



Measurements of the average lifetimes on the surface of the emitter have shown that such species persist on the emitter for a long period[23] (see below), reach thermal and charge equilibrium with the latter, and, on desorption, ionise via the surface ionisation mechanism.

Apart from the reactions examined, other reactions leading to the appearance of both ionising molecular fragments [for example, the products of the dehydration of the molecules—the species (M - H - 2*n*H) and (M - R - 2*n*H)] and non-ionising molecular fragments, can occur on adsorption of amines. However, the high efficiency of the formation of the ions $(M - H)^+$ and $(M - R)^+$ observed in many instances shows that the reactions involving the formation of the species (M - H) and (M -R) on adsorption of amines predominate and can take place with yields close to unity.

The above pattern in the adsorption of amine molecules is supported also by the low threshold temperatures for the ionisation of the radicals (M - H), which are even lower than the threshold temperatures for the ionisation of fluxes of Cs atoms having the same density[23]: if the adsorbed amine molecules were bound to the surface via many atoms, the species would have been desorbed at much higher temperatures.

The study of the surface ionisation of a series of *alkylhydrazines*[30,36] on emitters consisting of oxidised tungsten and molybdenum showed that, although the introduction into the molecule of the second heteroatom with formation of the >N–N< bond leads to some differences in the rules governing the formation of ions compared with amines, for example, it results in the formation of the ions M^+ [as a consequence of the decrease of the values of V_M for the molecules and the mutual approach of the ionisation potentials of the molecules and the radicals (M - H) compared with amines] and to the absence of lines of the ions derived from the associated species (apparently as a consequence of the conjugation between the heteroatoms), it does not alter the principal characteristics of the ionisation of nitrogen-containing organic compounds: mainly ions with saturated bonds are formed; they can be represented by ions with a quadrivalent positively-charged nitrogen atom having hybrid orbitals (Table 3). The efficiency of the ionisation of alkylhydrazines is higher; for example, the current density of the ions $(M - H)^+$ is approximately 10^{-2}–10^{-3} A Pa^{-1} cm^{-2} for trimethyl-, tetramethyl-, and dibutyl-hydrazines.

Comparison of data for the surface ionisation of a series of hydrazine derivatives[38], whose constituent atoms form the linkages >N–N=C< (hydrazones) –N=N– (azo-compounds) and >N–N=N–N< (tetrazenes), with data for the surface ionisation of alkylamines and alkylhydrazines shows that the ionisation efficiency of the radicals (M - H) decreases in the sequence amine > hydrazine > hydrazone > azo-compound [in the SI mass spectrum of tetramethyltetrazene the lines due to the ions $(M - H)^+$ are totally absent]; on the other hand, the ionisation efficiency of the molecules increases in this sequence (the mass spectrum of the primary ions of tetramethyltetrazene consists only of the lines due to the ions M^+). In contrast to hydrazines, the lines of $(M - Alk)^+$, caused by the ionisation of the species obtained on dissociation of the molecules at the N–C bond, are absent from the mass spectra of hydrazine derivatives. These differences can be accounted for by the decreased yield of reactions on the surface of the emitter which yield the above radicals rather than by the decrease in the ionisation potentials V_M of the molecules in the given series of compounds and the increase in the ionisation potentials of the radicals (M - H) and (M - Alk).

Table 3. The parameters of the SI mass spectra of certain alkylhydrazines[36].

Compound	*M*, a.u.	V_M, V	m_i, a.u.	Ion	Relative intensity, %	j, A cm^{-2}	T, K	V_i, V
1,1-Dimethyl-hydrazine	60	7.46 [45]	60	M^+	30	—		$7.35 \leqslant V \leqslant 7.8$
			59	$(M-H)^+$	100	$2\cdot10^{-10}$	1170	$\leqslant 7.4$
			45	$(M-CH_3)^+$	0.1	—		—
1-Ethyl-1-methyl hydrazine	74	—	74	M^+	60	—		$7.2 \leqslant V \leqslant 7.5$
			73	$(M-H)^+$	100	$5\cdot10^{-9}$	1200	$\leqslant 7.3$
			59	$(M-CH_3)^+$	8	—	»	—
			45	$(M-C_2H_5)^+$	0.7	—	»	—
Tetramethyl hydrazine	88	7.76 [46]	88	M^+	50	—		$\leqslant 7.2$
			87	$(M-H)^+$	100	$3.5\cdot10^{-8}$	1200	$\leqslant 7.15$
			85	$(M-3H)^+$	0.7	—	»	—
			73	$(M-CH_3)^+$	24	—	»	—
1,1-Di-n-butyl-hydrazine	144	7.57 [45]	144	M^+	6	—		$\leqslant 7.5$
			143	$(M-H)^+$	100	$2\cdot10^{-8}$	1150	$\leqslant 7.2$
			141	$(M-3H)$	15	—	»	—
			139	$(M-5H)$	5	—	»	—
			137	$(M-7H)$	0.7	—	»	—
			101	$(M-C_3H_7)$	100	$2\cdot10^{-8}$	1150	—
			99	$(M-C_3H_7-2H)$	15	—	»	—
			97	$(M-C_3H_7-4H)$	5	—	»	—
			87	$(M-C_4H_9)$	7	—	»	—
			85	$(M-C_4H_9-2H)$	2	—	»	—

The presence of a double bond in the molecules and the possible conjugation between the π-electrons and the electrons of the unshared pairs of the nitrogen atoms can result in the formation of a bond between the molecule and the emitter surface not only via the unshared pair of the nitrogen atom, as in the case of amines, but via the entire conjugated system of the electrons in the unshared pairs of the nitrogen atoms and the π -electrons. The adsorption of these molecules does not therefore entail a weakening of the β-bonds, as in the case of amines, and the yield of reactions with formation of the species (M - H) and (M - Alk) is correspondingly lower than in the adsorption of amines and their threshold ionisation temperatures are higher.

We may note that, although the surface ionisation efficiencies of hydrazine derivatives are smaller than those of the amines and hydrazines, they are nevertheless fairly high. Thus ionic current densities of approximately 10^{-4} A Pa^{-1} cm^{-2} can be obtained as a result of the surface ionisation of these substances.

The following differences between the characteristics of the surface ionisation of a series of *alkyl derivatives of phosphorus and arsenic* relative to amines have been discovered[47]:

1. The ionisation efficiencies of phosphines and arsines are much lower than those of amines and decrease in the series of compounds with heteroatoms in the sequence N > P > As. Thus, whereas in the ionisation of triethylamine the current density of the ions $(M - H)^+$ is $\sim 3 \times 10^{-2}$ A cm^{-2} Pa^{-1}, for triethylphosphine $j \cong 3 \times 10^{-4}$ A cm^{-2} Pa^{-1} and for tripropylarsine it is only 7×10^{-8} A cm^{-2} Pa^{-1}.

2. The decomposition of adsorbed molecules with formation of the radicals (M – R), which is characteristic of amines, does not occur in the case of phosphines and arsines: the intensity of the lines of the ions $(M - R)^+$ in the mass spectra of phosphines is low, while in the mass spectra of arsines the lines are altogether absent.

3. In the ionisation of phosphines and arsines the current of the ions M^+ is close in magnitude to that of the ions $(M - H)^+$, which indicates either a small difference between the ionisation potentials of the molecules and the radicals or a low yield of the reaction involving the formation of radicals in the adsorbed layer.

The characteristics of the surface ionisation of phosphines and arsines, relative to that of amines, enumerated above are associated with the difference between the electronic structures of the heteroatoms in these molecules. The orbitals of the unshared electron pair of the P and As atoms have a more pronounced *s* character than in the nitrogen atom, which should lead to a decrease of the probability of the formation of ions with an sp^2-hybrid structure. Furthermore, the P and As atoms have unoccupied *d* orbitals with relatively low energies, as a result of which they are capable of accepting electrons. Therefore in the adsorption of phosphines and arsines the withdrawal of the unshared pair of the heteroatom to the emitter can be accompanied by the capture of electrons from the emitter in the unoccupied *d* orbital. The latter should weaken the negative inductive effect of the adsorbed molecules and decrease the probability of their dissociation at the β-bonds.

V. THE FORMATION OF VIBRATIONALLY-EXCITED IONS IN THE SURFACE IONISATION OF ORGANIC COMPOUNDS AND THE CHARACTERISTIC FEATURES OF THEIR UNIMOLECULAR DECOMPOSITION REACTIONS

The mass spectra of almost all compounds contain, together with the narrow lines due to the primary ions which have been desorbed from the surface of the emitter and which have "reached" the collector of the mass-spectrometer, also broadened lines due to fragment ions—the products of unimolecular decomposition reactions of primary ions during their movement within the space of the mass-spectrometer.

A pair of lines due to fragment ions in the SI spectrum corresponds to each decomposition of the primary ions $m^+ \rightarrow m_1^+ + m_2$ (Fig.4): the decomposition of ions in the acceleration region within the ion source leads to the appearance of lines corresponding to the mass of fragment ions m_1, which have broadened in the direction of low masses or low energies of the ion; the same decomposition within the field-free region of the mass-spectrometer, between the accelerating electrodes of the source and the magnetic field zone, leads to the appearance in the mass spectrum of broadened lines due to ions with an apparent mass $m^* = m_1^2/m$.[48] The decomposition process can be unambiguously identified on the basis of the pair of lines recorded. By virtue of the high intensity of the lines due to the primary ions and the small number of lines in the SI mass spectra, it is therefore possible to identify the lines of the fragment ions whose intensity is many times smaller (by a factor of up to approximately 10^6) than the intensity of the lines due to the primary ions.

The ions obtained by surface ionisation obey the Boltzmann energy distribution as a function of the emitter temperature *T*; the energy is determined by *T* and the number of vibrational degrees of freedom of the ionising species [in the classical approximation the total vibrational energy stored in the species on the surface of the emitter before evaporation is $(3N-5)kT$, where *N* is the number of atoms in the species]. Some of the ions, whose total vibrational energy exceeds the energy of a decomposition reaction, can dissociate in the course of their travel through the mass-spectrometer.

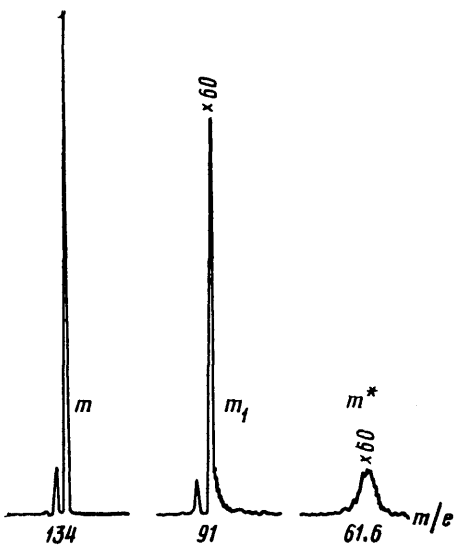


Figure 4. The lines due to the primary and fragment ions in the SI mass spectrum of benzyldimethylamine.

The unimolecular decompositions of the ions formed via surface ionisation are slow processes; the lifetimes of the ions are such that before decomposition they are able to execute more than 10^6–10^7 internal vibrations[34], which suggests that the decomposition reactions of the ions after their desorption from the surface of the emitter take place as a result of a statistical redistribution of the excitation energy within the ion; the energy being concentrated in such a way that a specific configuration of the activated complex, leading to its dissociation, is attained; the statistical theory of mass spectra can be applied to the description of such decomposition reactions[49].

The temperature variations of the ratios of the currents of fragment ions to the current of the parent ions make it possible to find the activation energies ε* for decomposition reactions which occur after the ions have moved for a specific time[24] (Fig.5). The true activation energy for the decomposition reactions or, in the case of direct decompositions, the bond dissociation energy in the ion can be determined from the values of ε* with the aid of the statistical theory of mass spectra[50,51].

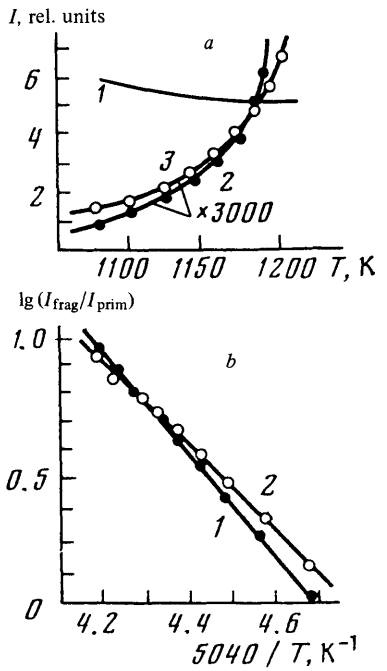


Figure 5. *a*) Temperature variation of the currents in the ionisation of diethylamine [*1*) for primary $(M - H)^+$ ions; *2*) for fragment ions with m_1 = 44 a.u.; *3*) for fragment ions with m^* = 26.9 a.u.; *b*) Arrhenius plots for the ratios of the fragment ion currents [*1*) m_1; *2*) m^*] to the primary ion current[32].

All the known types of unimolecular decomposition reactions of ions can be traced in the SI mass spectra: direct decompositions, decompositions with rearrangement, and multistage decompositions. In most cases the decomposition reactions of the ions obtained by surface ionisation belong to the type with rearrangements and to the multistage type and lead to the formation of stable fragments, which as a rule do not have unpaired electrons (Fig.6).

The mechanisms of the fragmentation of ions of different classes of organic compounds which have been deduced and the discovery of the characteristics of their decomposition pathways[33,36,38,47] are important for the purposes of the surface ionisation mass-spectrometry of organic compounds, since the primary ion can be "assembled" from the fragment ions (Fig.6).

Comparison of the decomposition reactions of ions obtained by surface ionisation (reliably identified experimentally), for which theoretical calculations have been made, with the decomposition reactions of the excited ions formed in collisions with electrons (with the mass spectrum generated as a result of ionisation by the electrons) can serve as a definite criterion of the applicability of the quasi-equilibrium theory to the description of the electron ionisation mass spectra[36,52] and in many instances can help in the determination of the pathways leading to the decomposition reactions on ionisation by electrons[38,52].

VI. SURFACE-IONISATION MASS-SPECTROMETRY OF ORGANIC COMPOUNDS

The set of results described constitutes the physicochemical basis of the method of the surface-ionisation mass-spectrometry (SIMS) of organic compounds. At the present

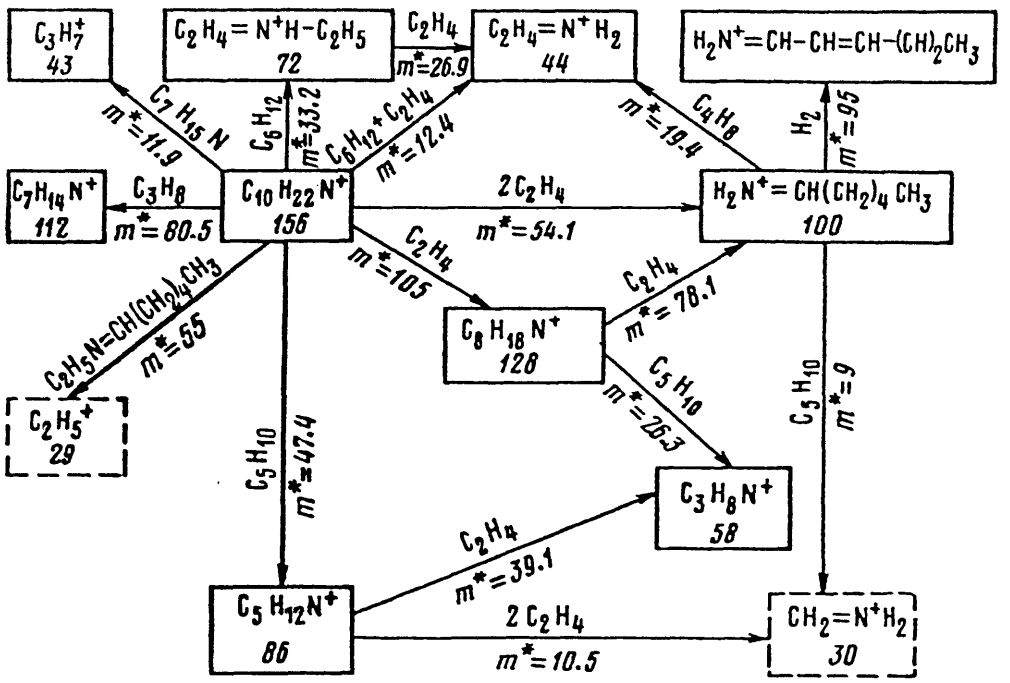


Figure 6. Unimolecular decompositions of the diethylhexylamine ions $(M - H)^+$.[33]

time SIMS can be applied only to specific classes of organic compounds with Group VA heteroatoms. However, the abundance and importance of these compounds are considerable. Certain fields of application of SIMS are examined below.

1. Application in Physicochemical Research

The following applications of SIMS are possible at the present time:

1. For the generation of fluxes of ions derived from organic compounds with considerable ion densities (up to 10^{-1}–10^{-2} A Pa^{-1} cm^{-2}). Their characteristic feature is a small scatter of the initial energies as a consequence of the Maxwell velocity distribution of ions as a function of the temperature of the emitter. The energy of the vibrational excitation of the ions can be readily regulated by altering the temperature of the emitter, which can be used in many problems, for example in the study of the influence of the vibrational excitation of ions on the kinetics of ion–molecule reactions.

2. For the detection of heterogeneous reactions from the chemical composition of the ions. The γ_i–T relations can be found by Eqns.(7)–(9) from the I_i–T relations for known $\beta_i(T)$ functions together with the concentration relations as a function of T for the ith species on the surface proportional to $\gamma_i(T)$. It is also possible to discover certain reactions with rearrangement on the surface, as can be seen from the ionisation of the molecules of ethyl-n-pentylamine, which have been partly converted into the molecules of *N*-ethylpiperidine[53].

3. For the estimation of the lifetimes of the vibrationally-excited ions with respect to unimolecular decomposition[34] and also for the determination of the activation energies ε for such decomposition reactions involving ions[24,50,51]. So far as we are aware, there are at present no other experimental methods for the determination of ε for reactions involving ions which would not require the knowledge of the thermochemical constants of the ions.

4. For the determination of the kinetic characteristics of the thermal desorption of species. We shall consider this problem in greater detail since it was not considered previously.

The kinetic characteristics of thermal desorption, namely the average lifetimes $\tau(T)$ of the adsorbed species relative to the desorption of ions and neutral species, the activation energies E^+ and E^0 for the desorption of these species, and the pre-exponential factors C and D in the equation for the flux of desorbed species $\nu^+ + \nu^0 = N[C \exp(-E^+/kT) + D \exp(-E^0/kT)] = N/\tau$ (N is the concentration of species on the surface) are the most important characteristics of the interaction of the species with the solid. The non-stationary processes ($\nu^+ + \nu^0 \neq \nu$), in which N varies with time, are used for their determination. The measured ionic currents are proportional to N.

The study of the ionisation of polyatomic organic molecules and radicals under non-stationary conditions is complicated by the simultaneous presence on the surface of the emitter of species of different composition, involved in reactions via many channels, which causes an additional variation of N_i as a function of time.

The present authors and their coworkers[23,54,55] analysed the possibility of determining the kinetic characteristics of the desorption of polyatomic species taking into account the reactions in the surface layer and using two isothermal methods for creating non-stationary conditions, which are explained in Fig.7: by modulating the potential at the surface of the emitter[56] (for $\beta_i > 0.1$) and by modulating the density of the incident molecular flux[57]. The solutions of the differential equations describing the time variation of N_i in each method made it possible to elucidate the significance of the measured characteristics, including those for the ionisation of molecules on inhomogeneous surfaces. As a rule τ is determined by the decrease of the number of species on the surface as a consequence of the processes occurring on the latter and is thus a quantity of practical importance. In many special cases it is possible to isolate $\tau_i^+(T)$ and $\tau_i^0(T)$ and correspondingly E_i^+ and E_i^0. In the case of non-uniform surfaces, all the parameters determined are effective; their magnitude approaches that of the characteristics of the desorption from the sections of their surface with the highest values of ϕ.

The quantities $\beta_i' = \beta_i/\{1 + [k_d/(k_0 + k_+)]_i\}$, where k_d, k_0, and k_+ are the rate constants for the dissociation and thermal desorption of the neutral ith species and the thermal desorption of their ions respectively, which are similar to the ionisation coefficients β_i, can be found from Fig.7 under conditions corresponding to the modulation of the potential with respect to the currents I_{i2} and I_{i1}. Evidently $\beta_i' < \beta_i$ and it is therefore possible to estimate the upper limit of the possible values of V_i from the β_i' with the aid of Eqns.(3) and (5). These estimates of V_i are more accurate than those based on the stationary currents defined by Eqns.(6) and (7) and do not require the knowledge of many quantities entering into these formulae which are difficult to determine.

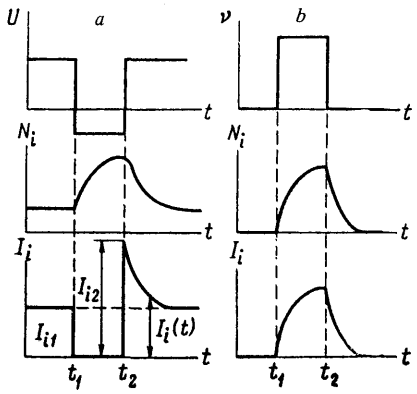


Figure 7. Illustration of the potential modulation method (*a*) (the rectangular waveform of the ion-arresting potential is switched on for the period from t_1 to t_2; ν = const.; T = const.) and of the flux density modulation method (*b*) (the molecular flux is introduced during the period from t_1 to t_2; U = const.; T = const.).

Table 4 presents the effective kinetic characteristics of the desorption and the values of β' obtained by the potential modulation method for several radicals formed from triethylamine, tributylamine, and tetramethyldiaminomethane when they are ionised on oxidised tungsten wires. These were the first determinations by the SI methods for species of such complex composition. Evidently the activation energy for the desorption of the ions is small. Because of this, the threshold temperatures for the ionisation of the radicals on oxidised tungsten wires are low; they are lower than for the ionisation of the corresponding fluxes of Cs atoms.

The quantities τ in the experimental temperature (T) ranges amount to tens–hundreds of milliseconds; such times are sufficient for the attainment of full thermal equilibrium in the adsorbed layer of species.

5. For the determinations or estimates of the ionisation potentials of species forming positive ions. The potentials V of species undergoing surface ionisation can be determined in different ways: (1) from the slopes of the plots of $\lg I_i = f(1/t)$ when the $I_i - T$ relation is exponential [Eqn.(8)] and the $\gamma_i - T$ relation may be disregarded[36,42]. It is then assumed that the ratio of the partition functions A_i is virtually independent of T. The error associated with this assumption is of the order of magnitude of $\sim kT$, which has been confirmed by the determinations of V for the molecules of aniline[42] and other compounds whose ionisation potentials had been determined by other methods[30]: (2) from the maximum current density and the corresponding temperature T. The value of β_i is found by Eqn.(6) and from it V_i is determined using Eqns.(3) and (5); it is then assumed that $\gamma_i(T) = 1$ and ν is found from the vapour pressure of the test substance in the apparatus. If the pressure is measured with an ionisation gauge calibrated with respect to nitrogen, then the experimental values of β are smaller than the true values and the ionisation potentials are correspondingly larger than the true values. Since the ionisation potentials V of radicals with Group VA heteroatoms are as a rule unknown[18], even estimates of their possible limiting values are of interest. The majority of the estimates have been made by this method. (3) From the values of β' obtained by the potential modulation method which is feasible for $\beta' \geq 0.1$.

Table 4. Kinetic characteristics of the thermal desorption of certain nitrogen-containing radicals from oxidised tungsten wires non-uniform with respect to emission.

Radical	E_+^* ±0,1, eV	lg C^*	β' (T)	E_0^* ±0,1, eV	lg D^*	Refs.
$C_2H_5NC_2H_4C_2H_5$	1.7	12.0±0.4	0.9 (900 K)	—	—	[23]
$C_2H_5NC_2H_5CH_2$	1.2	9.4±0.4	1.0 (840 K)	—	—	[23]
$(C_4H_9)NC_4H_8C_4H_9$	1.7	12.5±0.4	0.9 (900 K)	—	—	[23]
$(CH_3)_2NCHN(CH_3)_2$	1.0	8.3±1.0	0.99 (840 K)	2.1±0.1	12±1	[54]
$(CH_3)_2NCH_2$	1.5	11.0±1.0	0.88 (800 K)	1.5±0.1	10±1	[54]

Table 5 presents the values of V determined or estimated by the surface ionisation method. Evidently many radicals derived from nitrogen-containing compounds have relatively low ionisation potentials.

2. Applications in the Analytical and Structural Chemistry of Organic Compounds

The characteristic nature of the SI mass spectra of organic compounds and the simple rules governing the formation of ions and permitting the prediction of their composition in the mass spectra and the estimation of the current densities corresponding to the lines indicate the possibility of employing the SIMS in the analytical and structural chemistry of organic compounds. We shall examine certain possibilities of the analytical method based on the use of SIMS.[30,59]

The molecular weight of the substance analysed can be determined from the lines of the ions $(M - H)^+$ and, more rarely, from those of the ions M^+ and $(M + H)^+$. In all cases the characteristic form of the $I-T$ relations for each of these types of ions helps in their identification (Fig.2): the current of the ions M^+ as a rule increases with increasing temperature[30,36,47]. The mass numbers of the radicals R^i can be found from the $(M - R^i)^+$ lines; the current densities of the ions $(M - H)^+$ and $(M - R^i)^+$ yield information about the electronegativities of the substituents R^i; the $(M - H - 2nH)^+$ and $(M - R^i - 2nH)^+$ lines make it possible to assess the degree of saturation of the hydrocarbon substituents R^i. Finally, information about the structure of each primary ion can be obtained from the lines of its fragment ions (Fig.6).

Table 5. Ionisation potentials of certain molecules and radicals with Group VA heteroatoms.

Compound	Ionising species	V, V	Refs.
Ethylamine	(M+H)	$\lesssim$7.8	[32]
"	(M—H)	$\lesssim$8.3	[32]
Pentylamine	(M+H)	$\lesssim$7.7	[31]
"	(M—H)	$\lesssim$8.0	[31]
Aniline	M	7.65±0.07	[42]
Dimethylamine	(M+H)	$\lesssim$7.7	[30]
"	(M—H)	$\lesssim$8.3	[30]
Diethylamine	(M+H)	$\lesssim$7.2	[32]
"	(M—H)	$\lesssim$7.2	[58]
"	(M—3H)	$\lesssim$7.4	[32]
"	(M—CH_3)	$\lesssim$7.8	[32]
Piperidine	(M+H)	$\lesssim$7.6	[31]
"	(M—H)	$\lesssim$7.2	[31]
Pyridine	(M+H)	$\lesssim$7.5	[31]
Trimethylamine	(M—H)	$\lesssim$7.1	[30]
Triethylamine	(M—H)	$\lesssim$6.9	[32]
"	(M—3H)	$\lesssim$7.2	[32]
"	(M—CH_3)	$\lesssim$7.1	[32]
Dimethyloctylamine	(M—H)	$\lesssim$6.9	[30]
"	(M—C_7H_{15})	$\lesssim$7.1	[30]
Diethylhexylamine	(M—H)	$\lesssim$6.9	[30]
"	(M—CH_3)	$\lesssim$7.0	[30]
"	(M—C_5H_{11})	$\lesssim$7.0	[30]
Butyldipropylamine	(M—H)	$\lesssim$6.9	[30]
"	(M—C_2H_5)	$\lesssim$7.0	[30]
"	(M—C_3H_7)	$\lesssim$7.0	[30]
Ethyldimethylamine	(M—H)	$\lesssim$7.1	[34]
"	(M—CH_3)	$\lesssim$6.3	[54]
Allyldimethylamine	(M—H)	$\lesssim$7.1	[34]
"	[M—(CH=CH_2)]	$\lesssim$6.3	[54]
Tetramethyldiaminoethane	M	$\lesssim$7.8	[34]
"	(M—H)	$\lesssim$6.1	[54]
"	[M(CH_3)$_2$]	$\lesssim$6.3	[54]
"	(CH_3)$_2$N	$\lesssim$7.7	[34]
Cyano-*N*,*N*-dimethylaminomethane	(M—H)	$\lesssim$8.1	[30]
"	(M—CN)	$\lesssim$6.3	[34]
Benzyldimethylamine	(M—H)	$\lesssim$7.0	[34]
"	(M—C_6H_5)	$\lesssim$6.3	[54]
Dimethyl-*p*-nitrobenzylamine	(M—H)	$\lesssim$8.0	[34]
"	(M—$C_6H_5NO_2$)	$\lesssim$6.3	[54]
6-(9′-Acridinyl)-1-ethyl-1,2,3,4-tetrahydroquinoline	M	$\lesssim$7.2	[37]
2-Phenylbenzimidazole	M	7.0÷7.3	[37]
Methylhydrazine	M	7.53±0.08	[36]
"	(M—H)	$\lesssim$7.4	[36]
1,1-Dimethylhydrazine	M	7.35$\lesssim V \lesssim$7.8	[36]
"	(M—H)	$\lesssim$7.4	[36]
Trimethylhydrazine	M	7.2$\lesssim V \lesssim$7.5	[36]
"	(M—H)	$\lesssim$7.3	[36]
Tetramethylhydrazine	M	$\lesssim$7.2	[36]
"	(M—H)	$\lesssim$7.15	[36]
"	(M—CH_3)	$\lesssim$7.3	[36]
1-Ethyl-1-methylhydrazine	M	7.3$\lesssim V \lesssim$7.5	[36]
"	(M—H)	$\lesssim$7.3	[36]
1,1-Di-n-butylhydrazine	M	$\lesssim$7.5	[36]
"	(M—H)	$\lesssim$7.2	[36]
"	(M—C_3H_7)	$\lesssim$7.2	[36]
Acetone n-propylhydrazone	(M—H)	$\lesssim$7.1	[38]
Acetone isopropylhydrazone	(M—H)	$\lesssim$7.1	[38]
Azopropane	M	$\lesssim$7.2	[38]
"	(M—H)	$\lesssim$7.2	[38]
Tetramethyltetrazene	M	$\lesssim$7.1	[38]
Diethylphosphine	(M+H)	$\lesssim$7.8	[47]
"	(M—H)	$\lesssim$8.2	[47]
Triethylphosphine	(M+H)	$\lesssim$7.4	[47]
"	M	$\lesssim$7.8	[47]
"	(M—H)	$\lesssim$7.4	[47]
Tripropylphosphine	(M+H)	$\lesssim$7.8	[47]
"	M	7.8$\lesssim V \lesssim$8.2	[30]
"	(M—H)	$\lesssim$8.2	[47]
"	M	$\lesssim$8.3	[47]
"	(M—H)	$\lesssim$8.0	[47]

The small number of lines in the mass spectra facilitates the analysis of mixtures of substances. The degree of coverage of the emitter by the molecules of the test substances at temperatures above the threshold value for ionisation is low and the molecules in the adsorbed layer do not interact. Therefore the mass spectra of mixtures of different amines, hydrazines, and their derivatives are the sum of the mass spectra of the individual components[30,32]. The characteristic form of the $I-T$ relations for ions of each type makes it possible to distinguish, for example, the ions $(M_1 - H)^+$ from the ions $(M_2 - R)^+$ having identical masses. The high selectivity of surface ionisation can be used to determine minute trace amounts of amine impurities in mixtures of substances which are non-ionisable or weakly ionisable by surface ionisation. For example, tertiary alkylamines and their derivatives, present in amounts of $\geq 10^{-7}-10^{-8}$%, can be analysed with the aid of SIMS.[30]

The high efficiency of the surface ionisation of amines, hydrazines, and derivatives of substances of these classes is responsible for the high sensitivity of the analysis by the SIMS method, which significantly exceeds the sensitivity of the analysis using electron impact mass spectrometry. Thus, in the surface ionisation of tertiary amines and their derivatives, it is possible to obtain from an oxidised tungsten emitter having an area of 1 cm^2 currents of approximately 10^{-1} A Pa^{-1}, whereas currents of approximately $10^{-4}-10^{-6}$ A Pa^{-1} are obtained in the ion sources of mass spectrometers with electron ionisation. In this connection SIMS is promising for the analysis of bio-organic substances whose isolation even in microamounts requires as a rule the processing of a large amount of the initial material of biogenic origin. The study of the surface ionisation of the alkaloid allomatrine, vitamin B_2, riboflavin, and the acetylcholine mediator makes analysis simpler when SIMS is employed and its sensitivity is significantly higher than for mass spectrometry with ionisation by electrons[30,37]. The likelihood of SIMS being useful for the determination of the aminoacid sequence in peptides has been examined[30] and it has been concluded that, at least for relatively short peptides, the application of surface ionisation makes it possible to simplify the mass-spectrometric analysis and to increase significantly its sensitivity compared with the mass spectrometric analysis involving ionisation by electrons.

An important property of the ions obtained by surface ionisation, which distinguishes them from the ions formed using other ionisation procedures, is their definite energy characteristic: with equipartition of energy among the internal degrees of freedom, the ions have a Boltzmann distribution (as a function of the emitter temperature) with respect to the total internal energy. We believe that this property makes it useful to employ SIMS in the solution of one of the important problems of organic mass spectrometry—the determination of a relation between the reactivity of a compound and its mass spectrum.

The state of the knowledge of the characteristic features of surface ionisation of organic compounds and the possibility of employing the surface ionisation phenomenon for analytical and other purposes is at present sufficient to develop practical surface-ionisation mass spectrometry. The design of the surface-ionisation ion sources is simple; much experience has been gained in their development for mass spectrometers designed for isotope analysis. After a minor redesign of commercial mass-spectrometers (for example, by providing the mass spectrometer for isotope analysis with a system for the injection of the vapours of organic substances or by fitting the mass spectrometers for the analysis of organic compounds with a surface-ionisation ion source), they can be used also for the surface-ionisation analysis of organic compounds. The SI mass spectra of a series of cyclic amines obtained using the MI-1201 mass spectrometer[60,61]# can serve as an example of this.

VII. SURFACE-IONISATION DIODE DETECTORS OF ORGANIC COMPOUNDS

The high efficiency of the surface ionisation of amines, hydrazines, and their derivatives can be used for the sensitive and selective detection of microamounts of the above substances, for example, in air or in mixtures in the course of their chromatographic separation. It is then evident that detection can be achieved not only mass-spectrometrically but also with the aid of simple diode devices in which the overall ionic current between the emitter and the collector is measured[62,63].

The possibility of the practical realisation of surface ionisation in a diode device under the conditions of its separation not only *in vacuo* but also in air or in other gases has now been elucidated: ways have been found for the preparation of effective emitters operating in different media[27,64]; the designs of flow-type devices ensuring the virtually complete deposition of the substances analysed on the surface of the emitter have been developed[65,66]; the optimum operating conditions for diode detectors have been established[65,67]. The first surface-ionisation devices and highly selective methods for the detection of organic compounds belonging to the classes of amines, hydrazines, and their derivatives, which are unique as regards sensitivity, have been developed[64-67]. For example, with the aid of a diode surface-ionisation detector of simple design, it is possible to measure the content in air of tertiary alkylamines and their derivatives in an amount down to approximately $10^{-14}-10^{-15}$ litre^{-1}.[65]

The surface-ionisation detectors are designed for the following purposes.

1. For the monitoring of the contamination by gases of industrial premises as part of safety techniques. The "Valdai" surface-ionisation gas-analyser was developed in 1976 for the continuous monitoring of the contamination of industrial premises with gaseous diethylamine[68]. After appropriate calibration, it can be used also for the determination in air of microamounts of other secondary and tertiary alkylamines and their derivatives.

2. For the highly sensitive detection of leaks in hermetically-sealed compartments (containers, tubes, etc.). We may note that, when halogen leak-seeking devices are replaced by the more sensitive amine devices, the contamination of the upper atmosphere by Freon is prevented.

3. For gas chromatography. The surface-ionisation detector (SID) for gas chromatography has the following characteristics[65]: ionisation efficiency $\sim 4 \times 10^{-2}$ (with respect to triethylamine), background current $\sim 10^{-11}$ A, noise level $\sim(2-10) \times 10^{-14}$ A, threshold sensitivity $\sim 5 \times 10^{-15}$ g s^{-1} (with respect to triethylamine), linear range $\sim 10^4-10^8$, errors of readings $\leq \pm 5$% (with respect to triethylamine), continuous operation time ≥ 50 h, and selectivity with respect to hydrocarbons $\sim 10^5-10^8$.

#Unfortunately in the above investigations the authors, who obtained the mass spectra at an emitter temperature of approximately 2000 K, do not draw a distinction between the primary and fragment ions, which reduces the amount of information available from the SI mass spectra.

It is important that, in contrast to virtually all the existing selective detectors, the SID is selective with respect to the nature of the functional group containing the nitrogen atom and not with respect to the heteroatom itself[62]. It can therefore be used for the functional gas-chromatographic (GC) analysis of nitrogen-containing compounds[69]. Thus, using the simultaneous detection of the components at the outlet from the gas-chromatographic column by the SID and the flame-ionisation detector (FID), it is possible to determine the type of amino-group in aliphatic amines: when, for example, the Pye-Unicam FID is used, the SID/FID signal ratio is ~10^3–10^4 for tertiary amines, ~10^2 for secondary amines, and ~10 for primary amines[69,70].

The high SI efficiency with respect to tertiary alkylamines, significantly exceeding the SI efficiency for all other classes of organic compounds, can be used for the equisensitive detection with the aid of the SID of any organic compounds in mixtures in the course of their gas-chromatographic separation: by passing a tertiary alkylamine at a constant concentration together with the carrier gas through the gas-chromatographic column and by recording with the aid of the SID the variation of its volume concentration during the passage of the mixture components through the detector, it is possible to determine the volume concentrations of the components[71].

4. For the solution of any special problems in which the detection and identification of submicroamounts of amines and their derivatives is required, for example, of traces of toxic substances for the protection of the environment, for the identification of amines which are the active principles of an odour, for the determination of trace amounts of alkylamines and their derivatives in hermetically-sealed volumes, for the analysis of amines evolved by living organisms, etc.

In conclusion we may note that, when an additional initial stage involving the chemical conversion of the substances analysed into amines is used in the surface ionisation detection method, the latter can become universal and suitable for all substances capable of such conversion. For example, *N*-nitroso-compounds can be readily converted into amines by denitrosation; therefore the SID can be used for the determination of the contents of carcinogenic *N*-nitroso-compounds in food products and in the environment.

* * *

Thus it has only been recently established that organic compounds are capable of forming stable polyatomic positive ions via surface ionisation. As a result of the investigation of the characteristic features of this phenomenon for compounds with Group VA heteroatoms, extensive possibilities have arisen for the employment of surface ionisation in the physical and analytical chemistry of these compounds. The uniquely high sensitivity of the detection with the aid of surface ionisation of microamounts of many substances in the atmosphere and in other mixtures is of great practical importance.

There are already indications that compounds of other classes can also be ionised by surface ionisation[19,30,72–75]. There is no doubt that the further search for compounds capable of surface ionisation and the study of the characteristic features of their ionisation will significantly extend the applications of the phenomenon.

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Ioffe Physicotechnical Institute,
USSR Academy of Sciences, Leningrad