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SPRING COLLEGE IN CONDENSED MATTER
ON
"THE INTERACTION OF ATOMS & MOLECULES WITH SOLID SURFACES"
(25 April - 17 June 1988)

SURFACE IONIZATION OF MANY-ATOMIC PARTICLES AND ITS APPLICATION

(Part II)

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Surfase Ionization of Manyatomic Particles and its Applications

by

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Fig 1 [illegible]

Fig 2 [illegible]

Tab

SURFACE IONIZATION OF DIFFERENT CLASSES OF ORGANIC COMPOUNDS

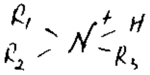
SI of I50 molecules of different classes of organic compounds has been studied by the present time, mainly these are the compounds with V^a subgroup heteroatom. The formulas for these classes are shown in the slide, the corresponding surface ionization efficiencies are given in the other slide. (See table 3 Lecture I)

It was found that what is ionized is primarily not the molecules of the original compounds but rather the products of their chemical transformations at the emitter surface (mainly of the dissociation reactions, and on metal emitters, only of them).

The SI mass spectra exhibit only few lines and may contain, irrespective of the emitter material used, such ion lines as $(M-H)^+$, $(M-R)^+$, $(M+H)^+$, $(M-H-nH)^+$, $(M-R-nH)^+$ and sometimes M^+, where M is the original molecule, H is the hydrogen atom eliminated from or added to it, n is an integer, R is the radical. The $(M+H)^+$ ions are observed only in the ionization on oxidized metals. ~~To provide a more complete picture of SI mass spectra,~~ I present in the Table 1 only, ~~Besides~~ the lines of primary ions (i.e. the ions produced by SI and reaching the mass spectrometer collector without breakup on the way). There are also ~~these~~ of secondary (fragment) ions. These ions are products of monomolecular breakup of the primary ions during their transit through the mass spectrometer. ~~I present also the schemes of their formation despite the fact that~~ All the aspects bearing on the formation in the course of SI of vibrationally excited metastable ions and on their monomolecular breakup will be analysed in the next lecture.

Thus surface ionization is preceded, as a rule, by a heterogeneous reaction involving the formation of the particle undergoing ionization. Note that the radicals (M-H) and (M-R) form as a result of rupture in the adsorbed molecule of the β -bond (C-H and C-R) relative to the nitrogen atom. The actual number of the $(M-H-nH)^+$ and $(M-R-nH)^+$ lines present depends on the length of the substituent alkyl chain. The maximum n corresponds to the dehydrogenation of alkyl radicals in which conjugated double bonds are formed. Note that the line intensity for even n is always much stronger than that for odd.

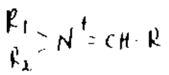
All the ions formed in the SI of organic compounds with nitrogen heteroatoms have, as a rule, an even number of electrons so that they can be approximated as ions with a quadrivalent, positively charged nitrogen having sp^3-, sp^2- or sp-hydrid orbitals. For instance, the $(M+H)^+$ ions of amines are similar to the ammonium ion NH_4^+ and have a quadrivalent nitrogen ion with sp^3-hydrid orbitals, namely,



$$\begin{matrix}R_1\\R_2\end{matrix}> \overset{+}{N} <\begin{matrix}H\\R_3\end{matrix}$$

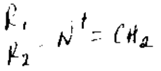
Note, that the amines are derivatives of ammonia NH_3 where radicals are substituted for the hydrogen atoms. The amines can be primary, secondary or ternary depending on the actual number of the substituted hydrogen atoms in the ammonia molecule.

The $(M-H)^+$ and $(M-R)^+$ ions have a nitrogen ion with sp^2 hybrid orbitals



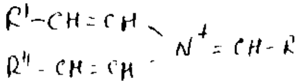
$$\begin{matrix}R_1\\R_2\end{matrix}> \overset{+}{N} = CH\cdot R$$

and



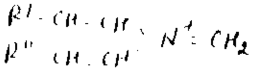
$$\begin{matrix}R_1\\R_2\end{matrix}> \overset{+}{N} = CH_2$$

and, finally, for the $(M-H-2nH)^+$ and $(M-R-2nH)^+$ ions we have



$$\begin{matrix}R'-CH=CH\\R''-CH=CH\end{matrix}> \overset{+}{N} = CH-R$$

and



$$\begin{matrix}R'-CH=CH\\R''-CH=CH\end{matrix}> \overset{+}{N} = CH_2$$

(obviously enough, the idea of the charge in ion being localised on one atom is oversimplified; indeed, the charge in a many-atomic ion is actually dictributed so that the structure of the $(M-R)^+$ ion, for instance, should rather be represented in the form

$$\begin{matrix}R_1\\R_2\end{matrix}> \overset{+}{N} = CH_2 \longleftrightarrow \begin{matrix}R_1\\R_2\end{matrix}> N - C^+H_2$$

with the highest probability for the charge to reside on the nitrogen atom. However for the sake of convenience we will in what follows consider the charge in an ion structure to be on the nitrogen atom).

The ionization efficiency depends on the character of the aminogroup involved. The ion current densities of similar radicals and associates grow substantially as the hydrogen atoms at the nitrogen become substituted by radicals. Indeed, the current densities of ethylamine $(M-H)^+$ ions are in the range of 10^{-5} A/Torr cm^2, those of diethylamine - $3\cdot10^{-1}$ A/Torr cm^2, and of triethylamine - 4 A/Torr cm^2.

The change in the ionization efficiency of alkylamine radicals correlates with that in the ionization potential of the particles undergoing ionization and can be explained qualitatively in the same way as this is done in the case of molecules, namely as due to a mutual influence of functional groups in the molecule within the framework of the inductive effect. For instance, alkyl radicals possess electron-donating properties which are more clearly pronounced than these of hydfogen atoms, they repel the nitrogen lone pair electrons stronger than the hydrogen atoms do, and attract weaker than is the case with the hydrogen atoms.

Table (Fig)

Effect of substituents in amine molecules on the composition and efficiency of ionization is illustrated clearly by the SI of trimethylamines $(CH_3)_2N-CH_2-R$, where R denotes substituents with different electronegativity: I - CH_3, II - $CH = CH_2$, III - $N(CH_3)_2$, IV - CN, V - C_6H_5, VI - n - $C_6H_4NO_2$. (see table 2)

The production efficiency of the $(M-H)^+$ ions depends substantially on the electronic and chemical properties of the substituents R, the $(M-H)^+$ current density varying within five decades (from 3 to $3 \cdot 10^{-5}$ A/Torr cm^2). This may be due not only to a difference in the ionization potentials of the (M-H) radicals of these compounds but to different yields of their formation on the emitter as well, i.e. to the difference in the values of γ. The observed qualitative correlation between the production efficiency of the $(M-H)^+$ ions and the Taft coefficients of the substituents permit one, however, a suggestion that the influence of the electronic and chemical properties of substituents on the yield in the reaction of abstraction of an easily migrating hydrogen atom from absorbed molecules is weak and that the effect of substituents affects primarily the magnitude of ν which depends substantially on the electron density distribution in the particle.

<u>The temperature dependences of the ion currents</u> of many-atomic particles are determined by the $\beta(T)$ and $\gamma(T)$ relation, so that the $I(T)$ plots can differ markedly from the $\beta(T)$ graphs.

The experimentally measured $I(T)$ plots do indeed differ from the $\beta(T)$ dependences. For all the alkylamines studied, the $I(T)$ dependences were found to be typical of each ion species (Fig. 1). The latter comes from the difference in the

Fig

dependences for each species of particles; indeed, reactions involving the formation of (M+H) associates proceed at lower temperature than is the case with the dissociation reactions, and the temperature threshold for the formation of (M-Alk) particles is substansially higher than the threshold of hydrogen atom elimination.

The considerable drop in the ion current observed with increasing T cannot be attibuted to the $\beta(T)$ dependence and originates obviously from the $\gamma(T)$ relation; for instance, as the temperature increases, the (M+H), (M-H) and (M-Alk) particles dissociate or the dissociation of the original molecules into smaller fragments becomes more pronounced.

The drop in the ion currents with decreasing emitter T may originate not only from the temperature threshold of SI when the ion current falloff is connected with the increasing concentration of adsorbed particles on the surface and the effect on the emitter work function and the heats of ion desorption, but also from the existence of a temperature threshold for the reactions involving the formation of the particles undergoing ionization. Which of these processes dominates in each particular case can be revealed, for example, by monitoring under the chosen experimental conditions the emitter work function as the temperature is varied.

It turned out that the decrease in the $(M+H)^+$ and $(M-H)^+$ amine ion currents at low temperatures is indeed connected with a decrease in the emitter work function, while throughout the temperature range where $I(T)$ dependence of the $(M-R)^+$ ion current was studied the work function did not change. One can thus conclude that the threshold on the $I(T)$ dependence of the $(M+H)^+$ and $(M-H)^+$ ions is due to a threshold temperature of the SI, the temperature threshold of the chemical reactions with formation of $(M+H)^+$ and $(M-H)^+$ particles lying below that of the SI for these particles. For the $(M-R)^+$ ions the threshold in the $\gamma(T)$ dependence play a dominant role.

A clear evidence for the effect of $\gamma(T)$ on the $I(T)$ dependences of the $(M-H)^+$ and $(M-R)^+$ ions was obtained by comparing the $I(T)$ of trimethylamine $(M-H)^+$ and dimethyloctylamine $(M-C_7H_{15})^+$ ions (Fig. 2). The trimethylamine (M-H) and dimethyloctylamine $(M-C_7H_{15})$ radicals are the same $(CH_3)_2NCH_2$ particles, however the $I(T)$ dependence of the ion current of these particles produced in the ionization of trimethylamine is illustrated by curve I, while that for the particles obtained in the ionization of dimethyloctylamine is illustrated by curve 2.

ig

Finally, direct evidence for the dominant role of $\gamma(T)$ in the $I(T)$ dependence of the $(M-R)^+$ ions was obtained by determining the $\beta(T)$ and comparing them with the $I(T)$ plots (Fig. 3). (The details of $\beta(T)$ determination will be discussed at the next lecture).

Fig

MECHANISM OF FORMATION OF ASSOCIATED OR PROTONATED $(M+H)^+$ IONS

All ionization studies of primary and secondary amines on oxidized metal emitters revealed lines of associated or protonated $(M+H)^+$ ions. On metal emitters, however, the $(M+H)^+$ ions did not form. The $(M+H)^+$ ions are produced also in the SI on oxidized metals of other classes of organic compounds, for instance, of pyridine, phenol and others. In cases where the SI mass spectra of tertiary alkylamine did have $(M+H)^+$ ion lines, they were weak and poorly reproducible.

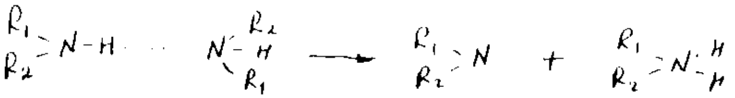
The $(M+H)^+$ ions are always observed at low emitter temperature, i.e. at the highest degrees of emitter surface coverage by adsorbed molecules, which still allow SI to be measured.

Fig $(I\sim\rho)$

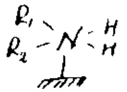
The bimolecular nature of the process ($I\sim\rho^2$) (see fig. 4) and the Maxwellian distribution of the $(M+H)^+$ ions in initial kinetic energy at the emitter temperature suggested that these ions form in the SI of (M+H) complexes (or associates). One had now to find the way in which the (M+H) complexes are produced on the surface.

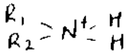
Note that the possibility of existence of stable H_3O and NH_4 complexes has been proved both experimentally and theoretically. Indeed, Ch.E.Melton observed desorption from a heated Pt surface of ammonium ions NH_4^+ and complexes NH_4 when ammonia was admitted to the mass spectrometer. Since the yield of these particles was found to increase with hydrogen admitted to the instrument, it was concluded that the complexes form at the platinum surface in the reaction $NH_4 + H_2 \rightarrow NH_4$. One can assume that the (M+H) complexes can form in this way also in the adsorption of amines. However admission to the mass spectrometer of H_2 or D_2 did not result in a growth of the $(M+H)^+$ ion current or an appearance of the $(M+D)^+$ ions.

It is known that because of the presence of a lone electron pair on the nitrogen atoms, the amines exhibit strongly pronounced protophobic and protophilic properties. Therefore the (M+H) complex formation is believed to result from the interaction on the emitter surface of amine molecules



Note that since the particles are adsorbed and thus participate in electron exchange with the surface, the adsorbed complex can be represented schematically in the following form



In the course of desorption, such a particle can "leave" an electron with the emitter and vaporize as a stable ion  with a quadrivalent, positively charged, sp^3-hybridized nitrogen.

This scheme is capable of accounting for the observed features of the $(M+H)^+$ ion formation, namely, (I) $(M+H)^+$ ions are produced at low T, i.e. under the conditions favorable for the formation and survival of the (M+H) complexes. The decrease in the current with increasing T results from a decrease in the concentration of the (M+H) particles in the adsorbed layer because of the decreasing molecule concentration as well as from the increasing probability of dissociation of the weakly bound (M+H) complexes; (2) Secondary amines are stronger bases than the primary ones and the $(M+H)^+$ current densities are higher in the ionization of the secondary amines; (3) In the case of ternary amines which are stronger bases than the primary ones the (M+H) complexes cannot form by autoassociation since the molecules do not have a hydrogen atom capable of participating in the production of such associates. As for the manifestation in the SI mass spectra of ternary amines of low intensity and poorly reproducible $(M+H)^+$ lines, they can be accounted for by the interaction of the amine molecules with the molecules of an impurity, e.g. water. This is supported by the observation of the $(M+H)^+$ ion line intensity in the ternary amine mass spectra being proportional to the residual water vapor pressure in the instrument and by the subsequent direct studies by T.Fujii of the effect of D_2O admission on the efficiency of protonated ion formation.

Another model is also possible. By this model, a protonated ion forms by proton transfer in a bimolecular reaction on the emitter surface, which can subsequently undergo thermal vaporization. This mechanism can operate only under conditions inhibiting or hindering electron exchange between the emitter and the particles adsorbed on it, as is the case, e.g., with the formation on the surface of zeolite of carbonium ions of triphenylmethyl in the adsorption of Ph_3CBr and subsequent vaporization of these ions from the heated zeolite surface (Rollgen). However while the oxidized W, Mo and Re belong to semiconductors, at the emission temperatures they reveal metallic properties; at any rate, the ionization of atoms and molecules with different V (ranging from 3.9 to 7.7 V) on the surface of oxidized tungsten was shown to follow the Saha-Langmuir relation, thus implying that charge equilibrium between the emitter and the adatoms with different obtains without any difficulties.

The SI of more complex amines, such as acridinyltetrahydroquinolenes and acridinylanilines with various substituents on the nitrogen atom (H, CH_3, C_2H_5), benzimidasoles, the alkaloid allomatrane and other follows the same lines in the ion formation as the SI of the lower amines.

1 table The Table 3 presents the SI mass spectra of some of them. The SI mass spectra of these compounds are seen to consist of the same characteristic set of ion lines as these for the lower amines, namely, $(M+H)^+$, M^+, $(M-H)^+$, $(M-R)^+$, $(M-H-2nH)^+$. All the ions with the exception of M^+ have an even number of electrons and can be represented as saturated-bond ions with a positive charge on the quadrivalent sp^2- or sp^3-hybridized nitrogen atom.

A study of the major features typical of the SI of amines and their derivatives permits one to formulate simple rules of ion formation which can be used to predict the ion composition in the SI mass spectra of amines and to evaluate the corresponding ion current densities. These rules stem from the high selectivity of SI with respect to the ionization potential of the particles being investigated; from the fact that the formation of bond-saturated ions, which in the case of amines can be represented as having a quadrivalent, positively charged hybridized nitrogen atom, is an energetically preferable process; finally, from the dependence of the V of the particles undergoing ionization on the electronegativity of the substituents.

(I) If the amine molecule contains a hydrogen-bonded carbon at position α to the nitrogen, then the $(M-H)^+$ ions will always form. The current density of these ions in the amine series increases as the hydrogen atoms on the nitrogen are replaced by alkyl or other electron-donating substituents. Electron-withdrawing substituents reduce substantially the $(M-H)^+$ current density. When ionized on oxidized W, the $(M-H)^+$ current densities γ

are $\sim 10^{-5} - 10^{-2}$ A/Torr cm^2 for primary amines, 10^{-1} A/Torr cm^2 for secondary, and $\sim$ (I-5) A/Torr cm^2 for tertiary amines. These current densities do not change much when ionization is carried out on emitters made of oxidized Mo and Re.

(2) If a molecule contains a carbon (or another atom) which is to the nitrogen, then the β (C-R)-bond breaks, this process being the more efficient the more stable is the radical R. The nitrogen-containing radicals thus formed are ionized yielding

$$\begin{matrix}R_1\\R_2\end{matrix}{>}N^{+}{=}CH_2$$

the current density of such ions depends on the electronegativity of the R_1 and R_2 substituents, as well as on the energy of formation of the radical R. If R_1 and R_2 are alkyl radicals, the $(M-R)^+$ current density is ~ 5 A/Torr cm^2.

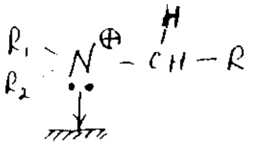
(3) The ionization of amines with alkyl substituents can be preceded by dehydrogenation of the molecules on the emitter, with single bonds being replaced by doudle ones. The ionization of the compounds thus produced yields $(M-H-2nH)^+$ and $(M-R-2nH)^+$ ions. In the ionization of amines with linear substituents, the line intensity of such ions is always substantially lower than that of the $(M-H)^+$ and $(M-R)^+$ ions. In the mass spectra of N-heterocyclic compounds, the line intensity of the $(M-H-2nH)^+$ ions leading to the ring aromatization can exceed that of $(M-H)^+$.

(4) Ionization of primary and secondary amines always reveals stable and producible $(M+H)^+$ lines originating from the ionization of the $(M+H)$ complexes which are produced in the autoassociation of the original molecules at the surface.

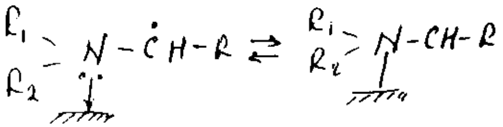
$(M+H)^+$ ions can be observed also in the ionization of ternary amines. Complexation is favored in this case by the presence in the mass spectrometer residual gas of water vapor or other protophobic compounds.

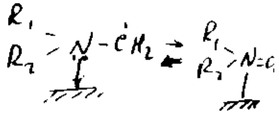
(5) Measurable currents of the molecular ions M^+ are observed in cases where the ionization potentials of the molecules do not exceed the emitter work function by more than ~ 2 eV; also, during their lifetime in adsorbed state the molecules should not undergo complete transformation into particles of a different chemical composition. This situation occurs with aromatic amines and N,N-heterocyclic compounds. However even when these conditions are met, the M^+ lines are revealed more clearly, as already mentioned, in the ionization of compounds which do not produce efficiently the $(M-H)^+$ ions.

These general features of ion production which are common for all amines and their derivatives and which do not depend on emitter material have been used in constructing a <u>scheme of adsorption of the amine molecules and of their reactions on the emitter.</u> Amine adsorption may be considered to occur via the formation of a coordination bonding with the adsorbent (it is known that the nitrogen lone pair in amine molecules is associated with the hybrid orbital, the amine molecule having a pyramidal structure with a nitrogen at the apex and being strongly oriented and polar. As the electron pair is being drawn out toward the emitter, a fractional positive charge forms on the nitrogen atom



Basing on chemical ideas of general nature and quantum-mechanical calculations, this should result in a substantial weakening of the β-bonds to the nitrogen. The rupture of these weakened (C-H) and (C-R) bonds leads to the formation on the heated emitter surface of (M-H) and (M-R) radicals:





(The (C-R) bonds break always at higher T than the (C-H) ones which happens at temperatures below the ionization threshold). Such particles, as shown by measurements of their mean lifetimes on emitter surface, reside for a comparatively long time on it, attain a thermal and charge equilibrium with it and undergo ionization by the SI mechanism when desorbing.

Apart from the above processes, the adsorption of amines can involve also other reactions resulting in the appearance of both ionizable particles, e.g. products of dehydrogenation of the molecules, such as (M-H-2nH) or (M-R-2nH), and unionizable fragments. However the high efficiency of $(M-H)^+$ and $(M-R)^+$ production observed in many cases shows that the reactions involving the formation of (M-H) and (M-R) particles in amine desorption dominate (at least at low degrees of coverage) and can proceed with close-to-unity yields.

The above picture of amine adsorption is supported by the following features of the process: the low threshold temperatures of (M-H) radical ionization which are even lower than those for Cs atoms at the same flux density; the $(M-H)^+$ and $(M-R)^+$ amine ions having heats of desorption lower than those of Cs^+ ions (if the adsorbed amine molecules were bound to the surface through many atoms, the particle desorption would occur at considerable higher T); the dependence of the efficiency of $(M-H)^+$ production on the steric accessibility of the nitrogen atom in the isomeric molecules of diethylbutylamines.

Until recently, a mass spectrometric study of surface ionization has been carried out on more than 150 organic compounds, among them hydrocarbons, lower ethers and alcohols, nitrocompounds, nitriles, phenols, acids, peroxides, amines and their various derivatives, including those of biogenic origin, hydrazines, hydrazones, azocompounds, tetrazenes, phosphines and arsines and a number of organometallic compounds. It has been shown experimentally that many-atomic particles, viz. molecules and radicals of organic compounds, are capable of forming ions by SI, their ionization obeying the relations following from the Saha-Langmuir expression. One has found that many organic compounds can be ionized efficiently by SI, determined the classes of compounds ionized on the surface with practically the highest possible efficiency; established the major features of ionization of the organic compounds containing heteroatoms of the V-A subgroup which permit prediction of the ion composition formed and the corresponding current densities.

The results exposed in this lecture show that studies of the SI of organic compounds not only broaden our ideas concerning the phenomenon proper but also increase substantially the possibilities of their application. Indeed, while earlier the SI was used to produce positive ions of about 70 elements, it is possible now to obtain by SI ions of many-atomic particles of diverse chemical composition and structure. Apart from this, new possibilities of using the phenomenon have been demonstrated, among them obtaining information on heterogeneous chemical reactions and their temperature behavior. Finally, one can now extend the SI technique to the investigation of physicochemical properties of a vast number of particles, namely, organic molecules and their radicals, as well as to the study of the process of their interaction with the surfaces of solids, - these problems will be discussed at the following lectures "Surface Ionization-Based Mass Spectrometry and Gas Analyzers of Organic Compounds. Application to physicochemical research and to the analytical and structural chemistry of organic compounds"; and "Nonstationary Processes in the Surface Ionization of Many-Atomic Particles".

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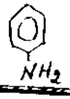
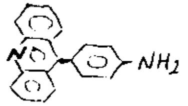
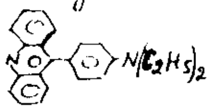
Tabl. 1 SI mass spectra

Compound	ions	j (A/Torr cm²)	T, K	vapor's pressure p
Ethylamine $C_2H_5NH_2$	$(M+H)^+$ $(M-H)^+$	$3\cdot10^{-7}$ $1\cdot10^{-5}$	600 1100	$p = 1\cdot10^{-7}$ Torr
Diethylamine $(C_2H_5)_2NH$	$(M+H)^+$ $(M-H)^+$ $(M-3H)^+$ $(M-CH_3)^+$	$1\cdot10^{-2}$ $9\cdot10^{-1}$ $1\cdot10^{-2}$ $2\cdot10^{-3}$	550 700 700 1100	$p = 1\cdot10^{-7}$ Torr
Triethylamine $(C_2H_5)_3N$	$(M+H)^+$ $(M-H)^+$ $(M-3H)^+$ $(M-CH_3)^+$	trace 4 $2\cdot10^{-2}$ 2.5	 550 600 1150	$p = 1\cdot10^{-7}$ Torr
Pyridine 	$(M+H)^+$	$3\cdot10^{-6}$	500	$p = 1\cdot10^{-2}$ Torr
Aniline 	M^+	$3\cdot10^{-4}$	1100	$p = 1\cdot10^{-7}$ Torr
4-(9'-Akridinil)-Aniline 	$(M+H)^+$ M^+	$3\cdot10^{-12}$ $2\cdot10^{-11}$ (A/cm²)	1150	evaporator's temperature t = 120 C
4-(9'-Akridinil)-diethylamine 	$(M+H)^+$ $(M-H)^+$ $(M-3H)^+$ $(M-5H)^+$ $(M-CH_3)^+$	 $7\cdot10^{-10}$ $3\cdot10^{-10}$ $1\cdot10^{-10}$ $1\cdot10^{-9}$ (A/cm²)	1150	t = 120 C

Tabl. 2 SI of trimethylamines $(CH_3)_2N-CH_2-R$. Effect of substituents

R	j (A/Torr cm²) of $(M-H)^+$ ions
$-CH_3$	1.2
$-CH=CH_2$	1.0
$-N(CH_3)_2$	0.9
$-CN$	$3\cdot10^{-5}$
$-C_6H_5$	3.0
$-n-C_6H_5NO_2$	$3\cdot10^{-5}$

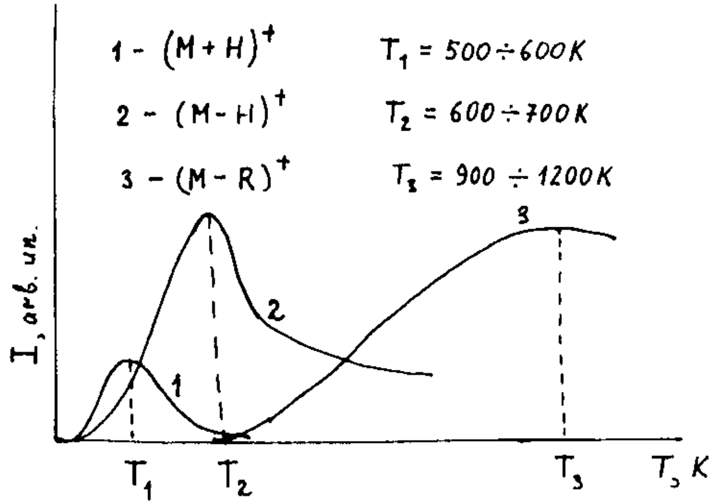


Fig. 1 The current temperature dependenses.

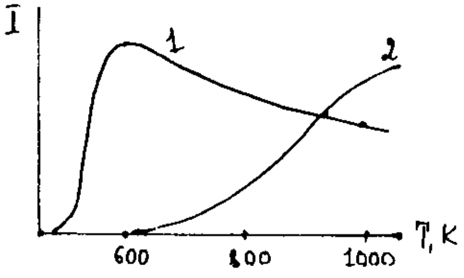


Fig. 2. I(T) dependences of the same ions $(CH_3)_2N^+=CH_2$

1 - $(M-H)^+$ from $(CH_3)_2ArCH_3$

2 - $(M-C_7H_{15})^+$ from $(CH_3)_2NC_8H_{17}$

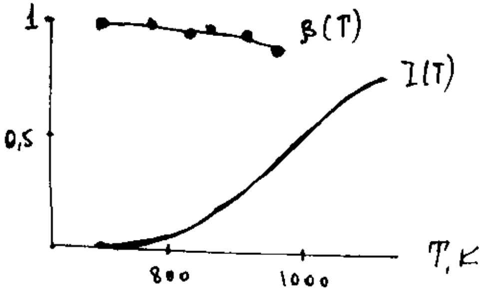
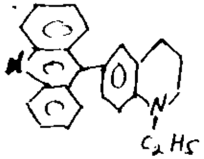
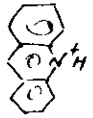
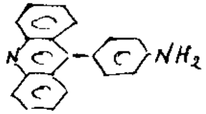
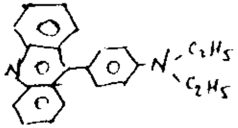
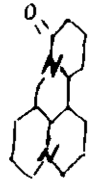


Fig. 3. I(T) and β(T) dependences of $(M-CH_3)^+$ from $(C_2H_5)_3N$.

Table 3 SI mass spectra.

Compound	m/e (mu)	Composition of ions	%	T, K	j (A/cm²), t, C of evaporater
	339	$(M+H)^+$	0,5	1000	$t \leq 90$
	338	M^+	4		
	337	$(M-H)^+$	11		
	335	$(M-3H)^+$	100		$j \approx 5 \cdot 10^{-8}$
	323	$(M-CH_3)^+$	1.5		
6-(9'-Akridinic)-1-ethyl-1,2,3,4-tetrahydrohinoline	180		2.0		
	271	$(M+H)^+$	15		$t \approx 120$
	270	M^+	100	1150	$j \approx 2 \cdot 10^{-11}$
	327	$(M+H)^+$	-	1150	
	326	M^+	26		$t \approx 120$
	325	$(M-H)^+$	100		
	323	$(M-3H)^+$	50		
	321	$(M-5H)^+$	17		
	311	$(M-CH_3)^+$	150		$j \approx 10^{-9}$
	249	$(M+H)^+$	-	1170	
	247	$(M-H)^+$	75		$t \approx 25$
	245	$(M-3H)^+$	80		$j \approx 10^{-8}$
	243	$(M-5H)^+$	100		
Allomatrane	241	$(M-7H)^+$	60		
	239	$(M-9H)^+$	20		
	237	$(M-11H)^+$	10		
	235	$(M-13H)^+$	2		

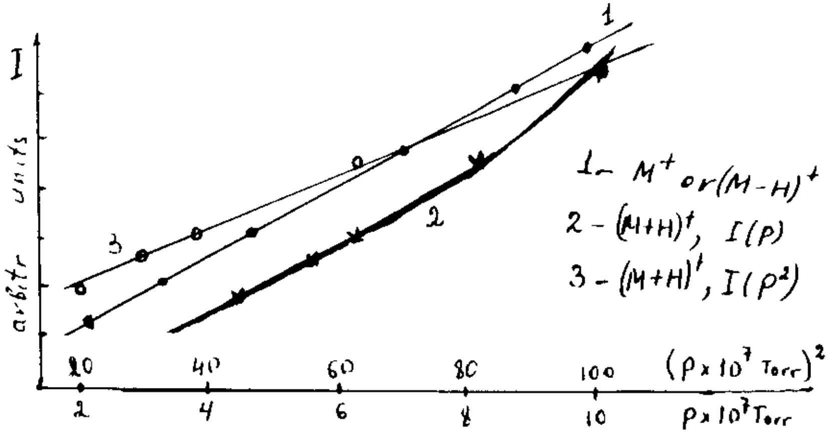


Fig. 4. The pressure dependences of the ion currents.

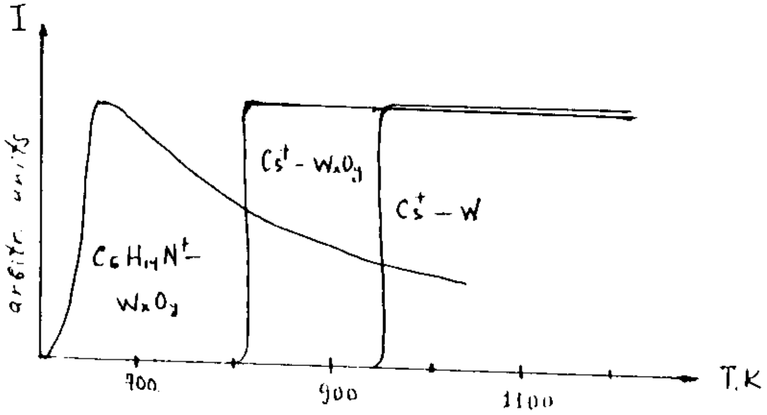


Fig. 5. The temperature dependences of the ion currents.