SURFACE-IONIZATION MASS SPECTROMETRY OF TERPENE HYDROCARBONS

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The surface ionizations of four terpene hydrocarbons (α-pinene, alloocimene, Δ^3-carene, and limonene) on oxidized tungsten wires and ribbons have been investigated. The mass spectra of the ions and the temperature dependences of the currents have been obtained, current densities have been estimated, and monomolecular decompositions of the metastable vibrationally excited ions have been found. The actions on the surface of oxidized tungsten leading to the formation of ionizing particles are considered. The ionizing potentials of the radicals (M − H) obtained on the splitting out of hydrogen atoms from the molecules have been estimated.

Surface ionization (SI) is the formation of ions during the thermal desorption of particles from a solid surface [1]. Not only ions of molecules directed to the surface of the thermoemitter but also the products of their thermal transformations in an adsorbed layer may be ionized. In the latter case, it is possible to judge from the mass spectra of the ions those reactions on the surface of the thermoemitter that lead to the formation of the ionized particles. In contrast to ionization by electrons, SI is an extremely selective process: only those molecules and the particles formed from them in the adsorption layer that do not undergo complete thermal decomposition and possess low ionization potentials not more than ∿2 eV greater than the work function of the emitter give measurable positive-ion currents [1].

TABLE 1. Mass Spectra Obtained by Surface Ionization (SI) and by Ionization with Electrons Having an Energy of 20 eV (EI)

m a.m.u	α-Pinene		Alloocimene		Limonene		Δ^3-Carene		Composition
	SI $T=980$ K	EI	SI $T=1150$ K	EI	SI $T=1100$ K	EI	SI $T=1150$ K	EI	
136	—	19	90	74	30	90	48	50	M
135	100	—	100	—	100	—	72	—	(M−H)
134	—	—	—	—	—	10	—	10	(M−2H)
133	30	—	70	—	30	—	28	—	(M−3H)
131	1	—	3	—	3	—	5	—	
129	1	—	1	—	1	—	1	—	(M−5H)
121	—	15	—	100	—	60	—	40	(M−CH_3)
119	6	—	7	—	4	25	100	20	(M−2H−CH_3)
117	—	—	—	—	—	—	—	2	
107	—	5	—	10	—	20	—	11	
106	—	—	—	—	—	—	—	3	
105	—	3	—	19	—	—	—	9	
95	—	—	—	—	—	10	—	10	
94	—	—	—	3	—	25	—	13	
93	—	100	—	18	—	100	—	100	(M−C_3H_7)
92	—	41	—	—	—	25	—	27	
91	—	24	—	7	—	5	—	17	
81	—	—	—	—	—	—	—	5	
80	—	5	—	—	—	5	—	20	
79	—	6	—	13	—	10	—	16	
77	—	4	—	2	—	15	—	10	
69	—	—	—	—	—	—	—	2	
68	—	—	—	—	—	75	—	4	
67	—	1	—	1	—	15	—	5	
55	—	—	—	—	—	—	—	3	
43	—	—	—	—	—	5	—	11	

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It has been established that of organic compounds those most effectively ionized by SI are amines, hydrazines, and other compounds with heteroatoms of subgroup Va [2]. Unsaturated hydrocarbons [3, 4] and, among them, terpene hydrocarbons [5], are ionized with a lower efficiency.

In those cases where the substances are ionized by SI its use has great advantages over other types of ionization, since it gives important information on a number of physicochemical properties of the compounds undergoing ionization: on the reaction that they undergo on the surface, on the temperature dependences of their yields, on the thermal stability of the radicals and associates formed on the surface and also of the desorbed ions; in addition, the ionization potentials of the particles ionized can be determined or estimated [2]. In view of the wide use of terpenes, investigations of their physicochemical properties are of great value.

It is also important that the use of SI in the analytical mass spectrometry of terpene hydrocarbons, as in the case of compounds with heteroatoms of subgroup Va, ensures the production of ionic mass spectra with few lines that are simpler than on the use of ionization by low-energy electrons and also the possibility of the ready identification of isomeric compounds in mixtures both from the composition of the lines in the mass spectra and from the temperature dependences of the ion currents [6].

Below, we give the results of an investigation of the SI of four $C_{10}H_{16}$ monoterpenes with different structures: alloocimene — an aliphatic compound with an open carbon chain; limonene — a monocyclic compound; and two bicyclic compounds — α-pinene and Δ^3-carene. Camphene — likewise a bicyclic compound, but with a different arrangement of the double bonds relative to the methyl groups — was not ionized by SI, in agreement with the established laws of the SI of terpene hydrocarbons. Ionization was carried out under vacuum conditions on heated oxidized tungsten wires and ribbons the thermoemission properties of which had already been studied [7, 8].

Table 1 gives the surface-ionization mass spectra of the primary ions of the four terpenes and, for comparison, the mass spectra of the same compounds on ionization by electrons with an energy of 20 eV. The surface-ionization mass spectra were obtained at the temperature T of the oxidized tungsten ribbons that were the optimum for the ionization of each compound. The intensities of the lines in Table 1 are expressed in percentages of the intensity of the main line; lines with relative intensities <1% are not given; the contribution of isotopic ions of other masses have been allowed for in the intensities of the lines.

It can be seen that the SI mass spectra and electron-ionization mass spectra differ substantially and that the SI mass spectra contain a far smaller number of lines than the mass spectra obtained by the ionization of the substances even by low-energy electrons. The set of lines in the SI mass spectra is characteristic: the main lines represent the ions M^+, $(M - H)^+$, and $(M - 3H)^+$; only in the case of Δ^3-carene does the main line have a mass, m = 119 a.m.u. representing $(M - 2H - CH_3)^+$. On comparing the mass spectra of α-pinene and Δ^3-carene the important role of the structure of the compound in the formation of the SI mass spectra appears clearly.

The differences in the SI mass spectra of isomeric terpenes are convenient for analytic purposes. The mass spectrum of α-pinene differs from the others by the absence of the M^+ line; that of Δ^3-carene by a main line with m = 119 a.m.u.; in alloocimeme the M^+, $(M - H)^+$, and $(M- 3H)^+$ lines differ little in intensity, while in limonene the $(M - H)^+$ line stands out sharply. An important circumstance for analysis is also the fact that the current densities in the lines of the SI mass spectra are fairly large (for the $(M - H)^+$ ions $I \approx (2\text{-}4)\cdot 10^{-6}$ $A/(cm^2\cdot Pa)$).

The mechanism of the formation of the radicals (M — H) on the surface of the emitter is of interest; the results of the ionization of these radicals is that the line of the $(M - H)^+$ ions is the main one in the mass spectra of all the terpenes that were ionized apart from the Δ^3-carene (in the mass spectrum of which the intensity of this line was not, however, low, amounting to ∿70%). It is assumed that the labile electrons of the π-bond of the adsorbed terpene molecule are drawn into the solid — the ion emitter. Then a partial positive charge is formed on the carbon atom at the multiple bond; this is compensated by a displacement of the electrons of the neighboring bonds, which leads to a weakening of the β-bonds in relation to the double bond and may cause the splitting out of the corresponding hydrogen atom [5]. Thus, for the formation of (M — H) radicals it is necessary that the terpene molecule should contain a methyl group in the α-position with respect to a carbon atom at a double bond. The four terpenes that were ionized satisfy this condition, while camphene, which did not ionize, does not. The rule given relates not only to terpene hydrocarbons but also to unsaturated hydrocarbons with different structures (aromatic and alicyclic [3, 4]). It must be fulfilled not only in the case of monoterpenes but also in the case of di-, tri-, and polyterpenes. In the adsorption of unsaturated hydrocarbons the double bond plays the same role at atoms of nitrogen, phosphorus, and other elements of subgroup Va in absorption and reactions on the surface of organic compounds with atoms of these heteroelements [2].

The ions $(M - H)^+$ and $(M - 3H)^+$, and also $(M - 5H)^+$, show the occurrence of the elimination of hydrogen atoms from the terpene molecules on the surface of the oxidized tungsten preceding SI. Such reactions lead to the formation of double bonds in cyclic compounds going as far as the aromatization of the rings (see, for example, the surface ionization of 1-methylcyclohexene [4] and of allomatrine in the case of compounds with a nitrogen heteroatom [9]). In general, as a rule, ions with even numbers of electrons are formed in SI, and not radical ions, since this is energetically less favorable [2]. From this point of view the reaction preceding the formation of the lines with m = 119 a.m.u. in the SI mass spectra of the terpenes can be represented as the splitting out of two H atoms with the formation of a double bond and the splitting out of one of the methyl groups present in the β-position with respect to this bond. The ion obtained in this way contains an even number of electrons. The high intensity of the line with m = 119 a.m.u. in the case of the SI of Δ^3-carene may be connected with the formation of a stable ion with its charge localized in the aromatized small ring.

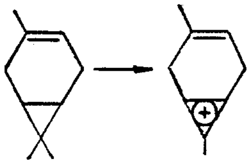

Figure 1 shows the temperatures dependences of the currents of the analogous $(M - H)^+$ ions of the various terpenes on their ionization at oxidized tungsten ribbons. It can be seen that the graphs of the relations $I/I_{max} = f(T)$ are different for different compounds, which is also convenient in the surface-ionization mass-spectrometric analysis of mixtures of terpenes.

From the values of the ion current densities obtained by SI it is possible to estimate the ionization potentials V of the particles undergoing ionization (including those formed in surface reactions) with the aid of formulas for current densities that are known for this type of ionization [1, 2]. According to such estimates, the values of V for the (M − H) radicals of all four compounds are less than 7.7 eV.

In the SI mass spectra obtained with the aid of static magnetic mass spectrometers of the sector type, as in the electron-ionization mass spectra, there are lines caused by the decomposition of metastable ions [2, 10]. Under these circumstances, decomposition in the field-free space of the mass spectrometer leads to the formation of lines broadened on both sides with effective masses $m^* = m_1^2/m$ (where m is the mass of the primary metastable ion, and m_1 is the mass of the secondary ion formed on its breakdown; in the majority of cases, m^* is a fractional magnitude). Decomposition in the zone of acceleration in the iron source leads to the appearance of lines with mass m_1 broadened in the direction of lower masses. Thanks to these two types of lines, connected by the relation given, in SI mass spectra the pathways of the decomposition of the metastable ions are shown reliably, this also being aided by the fewness of the lines of the mass spectra and the rarity of the occurrence of the superposition of the primary and secondary lines. The efficacy of decomposition increases with a rise in the temperature of the ion emitter, since decomposition must take place as a consequence of the fluctuational accumulation on individual bonds of the vibrational energy imparted by the heat emitter to all the bonds of the particle absorbed in it. It is possible to find the energy of the bond breaking in the ion from the temperature dependence of the efficiency of decomposition [2].

Table 2 gives information, refined in comparison with [5], on the decomposition of the vibrationally excited metastable M^+ and $(M - H)^+$ ions of the four terpenes. The relative efficiencies of decomposition are low, with the exception of those of the radical ions M^+.

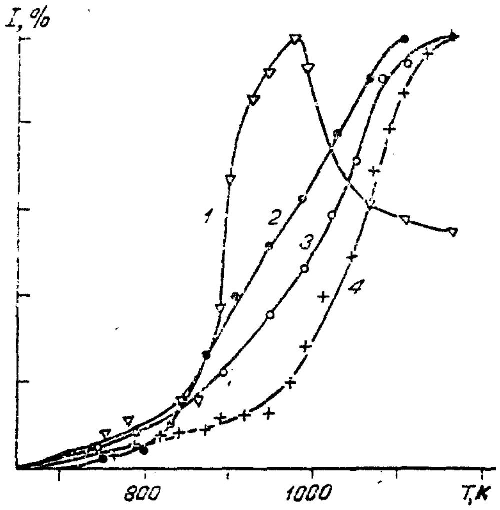

Fig. 1. Temperature dependences of the currents of the $(M - H)^+$ ions of: 1) α-pinene; 2) Δ^3-carene; 3) limonene; 4) alloocimene.

TABLE 2. Decompositions of Metastable Ions at the Given Emitter Temperatures T (K)

Substance, $C_{10}H_{16}$, M = 136 a.m.u.	Masses recorded	Relative intensities, % of the line of the metastable ion	Identification of the decomposition
α-Pinene $T=980$	$m_1 = 107$ $m^* = 84{,}7$	0,1 0,1	$(M-H)^+ \rightarrow C_8H_{11}^+ + C_2H_4$
	$m_1 = 93$ $m^* = 64{,}1$	0,1 0,1	$(M-H)^+ \rightarrow C_7H_9^+ + C_3H_6$
Alloocimene $T=1150$	$m_1 = 121$ $m^* = 107{,}6$	0,1 11,1	$M^+ \rightarrow C_9H_{13}^+ + CH_3$
	$m_1 = 43$ $m^* = 13{,}6$	0,1 —	$M^+ \rightarrow C_3H_7^+ + C_7H_9$
	$m_1 = 107$ $m^* = 84{,}7$	— 0 1	$(M-H)^+ \rightarrow C_8H_{11}^+ + C_2H_4$
	$m_1 = 93$ $m^* = 64{,}1$	0,1 0,1	$(M-H)^+ \rightarrow C_7H_9^+ + C_3H_6$
Δ^3-Carene $T=1150$	$m_1 = 121$ $m^* = 107{,}6$	9,6 4,6	$M^+ \rightarrow C_9H_{13}^+ + CH_3$
	$m_1 = 93$ $m^* = 63{,}6$	2 5 4,4	$M^+ \rightarrow C_7H_9^+ + C_3H_7$
	$m_1 = 43$ $m^* = 13{,}6$	2,1 —	$M^+ \rightarrow C_3H_7^+ + C_7H_9$
	$m_1 = 107$ $m^* = 84{,}7$	— 2,1	$(M-H)^+ \rightarrow C_8H_{11}^+ + C_2H_4$
Limonene $T=1100$	$m_1 = 121$ $m^* = 107{,}6$	1,3 3,3	$M^+ \rightarrow C_9H_{13}^+ + CH_3$
	$m_1 = 43$ $m^* = 13{,}6$	3,3 —	$M^+ \rightarrow C_3H_7^+ + C_7H_9$
	$m_1 = 107$ $m^* = 84{,}7$	— 1,5	$(M-H)^+ \rightarrow C_8H_{11}^+ + C_2H_4$
	$m_1 = 93$ $m^* = 64{,}1$	2,1 1,2	$(M-H)^+ \rightarrow C_7H_9^+ + C_3H_6$

Because of the even numbers of electrons in the $(M - H)^+$ ions they are more stable than the $M^{+\cdot}$ ions. The radical ions $M^{+\cdot}$ generate radicals in their breakdowns, while the ions $(M - H)^+$ generate only stable, nonradical, fragments.

Attention is attracted by the fact that, in the decomposition of metastable vibrationally excited ions obtained by the SI method, secondary ions are obtained at the same masses as some of their main dissociative ions in electron-ionization mass spectra (see Tables 1 and 2). As has been shown in [11], this indicates that in the case of impact ionization the energy of excitation of molecules by electrons passes into vibrational energy by the same pathways as in the thermal excitation of molecules.

EXPERIMENTAL

The experimental technique and procedures that have been described in detail in [12] were used. A high-vacuum static magnetic spectrometer of the sector type had a duplicated ion source with ionization of two types: with surface ionization and with electron ionization. The instrument included an energy analyzer for measuring the energy distributions of the ions formed by thermal ionization at an emitter in order to answer the question of thermal equilibrium in the adsorption layer. This was necessary in order to establish the possibility of using the formula of surface ionization for the current I of ions with the i-th composition,

$$I_i = \frac{e\nu\gamma_i(T)S}{1 + B_i \exp[e(V_i - \varphi)/kT]}$$

[1, 2] to estimate the ionization potentials V_i of the corresponding radicals. In this formula, e is the elementary charge; ν is the specific flux of molecules to the surface of the emitter; $\gamma_i(T)$ is the yield of the reaction forming radicals with the i-th composition on the surface of the emitter; S is that part of its area from which the current of the i-th ions measured during the experiments, $I_i(T)$, is derived; B_i is a coefficient close in magnitude to unity; V_i is the ionization potential of the particles of the i-th type; φ is the work function of the ion emitter; k is Boltzmann's constant; and T is the temperature of the emitter.

Estimates of V_i were made in the approximations $B_i = 1$ and $\gamma_i(T) = 1$, which lead to an overestimate of the values of V_i. The specific flux of molecules, ν, was determined from the vapor pressure of the substance on its admission to the ion source with the aid of the well-known relation $\nu = 4.67 \cdot 10^{24} \cdot P/(MT_V)^{1/2}$, where P is the vapor pressure, Pa; M is the molecular mass of substance; and T_V is the temperature of the vapor. The additional diode device described in [5] was attached to the ion source for measurements of $I_i(T)$ at an accurately known area S of the emitting surface.

Vapors of the chromatographically pure substances were admitted to the ion source from a metal inlet system with autonomous pumping out.

The mass spectrum was scanned by means of the magnetic field.

SUMMARY

The surface ionization of four monoterpenes on oxidized tungsten has been investigated. The mass spectra have few lines and are different for different compounds. The temperature dependences of the ion currents of identical masses also differ.

Terpene molecules undergo the elimination of hydrogen and the aromatization of rings on the heated surface.

The main lines in the mass spectra are those of the $(M - H)^+$ ions; the decomposition of metastable $(M - H)^+$ ions is unlikely.

The ionization potentials of the radicals (M − H) have been estimated.

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CYCLIZATION AND REARRANGEMENTS OF DITERPENOIDS.

VIII. PRODUCTS OF DEHYDRATION OF (1S,2S,7S,10R,11S,12S)-2,6,6,10,12-PENTAMETHYLTETRACYCLO[10.2.1.$0^{1,10}$.$0^{2,7}$]-PENTADECAN-11-OL BY PHOSPHORUS OXYCHLORIDE

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On the dehydration of (1S, 2S, 7S, 10R, 11S, 12S)-2,6,6,10,12-pentamethyltetracyclo[10.2.1.$0^{1,10}$.$0^{2,7}$]pentadecan-11-ol by phosphorus oxychloride in pyridine a mixture of three hydrocarbons is formed: the known (1R, 2S, 7S, 10S, 11R, 12S, 13S)-2,6,6,10,12-pentamethyltetracyclo[10.2.1.$0^{1,10}$.$0^{2,7}$.$0^{11,13}$]pentadecane and the previously undescribed (1R, 2S, 7S, 10S, 11S)-2,6,6,10,12-pentamethyltetracyclo[9.2.2.$0^{1,10}$.$0^{2,7}$]pentadeca-12-ene and (1R, 2S, 7S, 10S, 11S)-2,6,6,10-tetramethyl-12-methylenetetracyclo[9.2.2.$0^{1,10}$.$0^{2,7}$]pentadecane, based on a new carbon skeleton.

We have previously [1] investigated the products of the dehydration of (1R, 2S, 7S, 10S, 12S, 13S)-2,6,6,10,12-pentamethyltetracyclo[10.2.1.$0^{1,10}$.$0^{2,7}$]pentadecan-13-ol (I) – one of the two alcohols formed on the electrophilic cyclization of a number of labdane diterpenoids. Continuing this work, in the present communication we give information on the products of the dehydration of (1S, 2S, 7S, 10R, 11S, 12S)-2,6,6,10,12-pentamethyltetracyclo[10.2.1.$0^{1,10}$.$0^{2,7}$]-pentadecan-11-ol (II) – an isomer of the alcohol (I) – by phosphorus oxychloride.

In this case, the reaction gave with fairly high yield a mixture of only three hydrocarbons, which were separated by chromatography on silica gel impregnated with silver nitrate and by crystallization. The least polar hydrocarbon proved to be (1R, 2S, 7S, 10S, 11R, 12S, 13S)-2,6,6,10,12-pentamethylpentacyclo[10.2.1.$0^{1,10}$.$0^{2,7}$.$0^{11,13}$]pentadecane (III), which is also formed in the dehydration of alcohol (I) [1]. The product next in polarity, containing a trisubstituted double bond, was, judging from its IR and PMR spectra and chromatographic behavior, identical with hydrocarbon A obtained in the dehydration of alcohol (I), the structure of which has remained unelucidated [1]. The most polar substance eluted from the column, having a hemicyclic double bond was identical with hydrocarbon B – another product of the dehydration of alcohol (I) [1] with an undetermined structure.

On the basis of the proofs given below, it was established that hydrocarbon A is (1R, 2S, 7S, 10S, 11R)-2,6,6,10-12-pentamethyltetracyclo[9.2.2.$0^{1,10}$.$0^{2,7}$]pentadeca-12-ene (IV), with a new carbon skeleton. On ozonization it gave two products: (1R, 2S, 7S, 10S, 11R, 12R)-2,6,6,10,12-pentamethyltetracyclo[9.2.2.$0^{1,10}$.$0^{2,7}$]pentadecan-12-one (V) and (1S, 2S,

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