SURFACE IONIZATION OF THE RADICAL $\mathrm{C_4H_{10}N}$

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SURFACE IONIZATION OF THE RADICAL $C_4H_{10}N$

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When molecules of diethylamine $C_4H_{11}N$ interacted with the surface of heated tungsten and oxidized tungsten in weak electric fields $\mathcal{E} < 10^5$ V/cm, emission of ions of the radicals $C_4H_{10}N^+$ was observed. The ion-current density from oxidized tungsten reached $3 \cdot 10^{-8}$ A/cm^2 at diethylamine pressures $p \sim 10^{-7}$ torr as measured by an ionization manometer; the dependence of the ion current i on the emitter temperature T passed through a maximum (^{1}).

In the present communication we present results of a study of the mechanism of ionization of the radical, an estimate of the value of its ionization potential V, and the energy of the C–N bond in its ion.

If the radicals $C_4H_{10}N$ are ionized by surface ionization, then the charge ratio in the desorbed fluxes is determined by the Saha–Langmuir formula (^{2}), while the magnitude of the current and the dependence $i(T)$ are determined by the magnitude and temperature dependence of the ionization coefficient β and of the yield of the reaction forming the radical on the emitter γ (^{3}). In this case V can be estimated.

The Saha–Langmuir formula can be used under the condition of thermodynamic equilibrium in the system emitter–layer of adsorbed particles (adlayer). Thermodynamic equilibrium implies charge, chemical, and thermal equilibrium between the emitter and the adlayer. Thermal equilibrium in the case of polyatomic particles includes the equilibrium distribution of particles in translational, rotational, and vibrational motion of the particles as a whole, as well as over all types of internal motion of the atoms in the particle (^{4}).

We have experimentally studied the distribution of $C_4H_{10}N^+$ ions over the normal components of the velocities of translational motion during ionization of diethylamine on oxidized tungsten. The method of current-voltage characteristics in the region of electric fields retarding the ions was used (the retarding-potential curves method (^{5})). The retarding curves of $C_4H_{10}N^+$ ions were compared with the retarding curves of Cs^+ ions formed by surface ionization on oxidized tungsten under the same experimental conditions. It is well known that the energy

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

distribution of Cs^+ ions formed by surface ionization is Maxwellian, with the temperature of the emitter (^{5,6}).

From the retarding curves one also determines the contact potential difference U_k between the emitter and the analyzing electrode, from the magnitude of which one can judge the constancy of the emitter work function φ at all T and p, as well as the dependence $\varphi(T)$.

To obtain retarding curves, electrodes with an ion-retarding potential were introduced between the exit diaphragm and the multiplier in the mass analyzer of work (^{1}) (Fig. 1). These electrodes were made of fine-mesh screens with a transparency of $\sim 85\%$. The residual pressure in the instrument was $(3 \div 5) \cdot 10^{-8}$ torr; the admission of diethylamine vapor was carried out up to $p \sim 2 \cdot 10^{-7}$ torr as measured by the ionization manometer. The emitters were thermally purified and recrystallized tungsten wires, which were oxidized with oxygen and reduced by heating in vacuum.

Figure 2 shows typical retardation curves for Cs^+ ions and $C_4H_{10}N^+$ ions desorbed from oxidized tungsten, as well as Cs^+ ions from a cleaned tungsten surface. The slopes of the straight-line portions

Fig. 1. Electrode arrangement in the mass spectrometer for studying retardation curves:
1—filament; 2—focusing electrode; f_1 and f_2—focal planes of the mass spectrometer; S_1 and S_2—slits determining the resolving power; 3—electrodes with the retarding potential; 4—multiplier receiver; 5—cesium evaporator.

of the curves for Cs^+ and $C_4H_{10}N^+$ at identical T of oxidized tungsten coincided to a good degree of accuracy and were sufficiently sensitive to changes in the emitter temperature. Thus, it has been shown that the distribution of $C_4H_{10}N^+$ ions over translational velocities is an equilibrium one.

Fig. 2. Retardation curves of Cs^+ ions (a) and $C_4H_{10}N^+$ ions (b).
1, 2, 3—oxidized tungsten at $T = 800^\circ$ K (1) and 1000° K (2); 3, 4—tungsten at $T = 2150^\circ$ K (3) and 2400° K (4). $\Delta\varphi = \Delta U_k = 1.4$ V.

The distribution of translational velocities is established as a result of vibrations of the particles normal to the surface and, consequently, the lifetime of adsorbed particles on the surface is large compared with the period of one vibration, including in the direction of individual bonds. Conse-

···the rate of establishment of equilibrium among particles in the gas phase is

Fig. 3. Dependence $\lg \frac{i_{m^*}}{i_{M=72}} = f(1/T)$ during ionization of diethylamine on oxidized tungsten

Figure 3: Fig. 3. Dependence $\lg \frac{i_{m^*}}{i_{M=72}} = f(1/T)$ during ionization of diethylamine on oxidized tungsten

such that the slowest relaxation processes prove to be the vibrational processes (^{7}). On the surface of the emitter the relaxation processes must proceed faster than in the volume, because of the smallness of the mean free paths of the particles on the surface. Thus, the ionization of diethylamine radicals formed as a result of reactions on the surface, owing to the equilibrium distribution of ions with respect to kinetic energy, should be regarded as an equilibrium process. There is one further additional proof of this.

At high sensitivity in the registration of currents, a broadened line is observed in the ion spectrum, due to a "metastable ion" with apparent mass $m^* = 25.8$. This line corresponds to $C_2H_5N^+$ ions with $M/e = 43$, which are formed in the drift space between the accelerating electrode of the source and the magnetic-field zone during the decay of ions

$$C_4H_{10}N^+ \to C_2H_5N^+ + C_2H_5 \quad (m^* = 43^2/72 \approx 25.7).$$

Fig. 3. Dependence $\lg \frac{i_{m^*}}{i_{M=72}} = f(1/T)$ during ionization of diethylamine on oxidized tungsten

Figure 3 shows the dependence $\lg i_{m^*}/i_{M=72} = f(1/T)$. The slope of such plots corresponds to a C–N bond energy in the $C_2H_{10}N^+$ ion of ~ 1.5 eV. The observed ratio in the spectrum of the intensities of the $C_4H_{10}N^+$ and $C_2H_5N^+$ lines, equal to $3 \cdot 10^4$ at 1150° K and $1 \cdot 10^5$ at $T = 950°$ K, corresponds to that expected for the indicated bond energy with a Boltzmann distribution over the bond energies of the $C_2H_5N^+$ ions.

It may therefore be regarded as proved that the $C_4H_{10}N^+$ ions are formed by surface ionization. The bell-shaped form of the dependence $i(T)$ can be connected only with the dependence $\gamma(T)$ (^{1}), since measurements of the contact potential difference at different T did not reveal a decrease in φ with increasing T. From the Saha–Langmuir formula it follows that

$$i(T) = \frac{e\nu(T)}{1 + \frac{1}{A(T)} \exp \frac{e(V - \varphi)}{kT}}, \tag{1}$$

where e is the charge; k is the Boltzmann constant; $A(T)$ is the ratio of the statistical sums of the ionic and neutral states of the radicals, and $\nu(T) = v\gamma(T)$

is the total flux of neutral and charged radicals desorbed from the surface at a constant flux of molecules v to the emitter. If the emitter is inhomogeneous and $e(V-\varphi_{\max}) \gg kT$, then

$$i(T) \approx e\nu(T)A^*(T)\exp\frac{e(\varphi^*-V)}{kT}, \tag{2}$$

where φ^* and A^* are the effective values of φ and A (^{2}).

The absolute magnitudes of $i(T)$, $\nu(T)$, and $A(T)$ are unknown, and we estimated V by comparing the currents of $C_4H_{10}N$ ions formed at selected T on tungsten and on oxidized tungsten at the same pressure of diethylamine in the apparatus. Introducing, respectively, the subscripts W and O, and applying formula (1) for the oxide and formula (2) for W, we obtain

$$\frac{i_W}{i_O} = \frac{\nu(T)_W}{\nu(T)_O}\left\{A^*_{\mathrm{TW}}\exp\frac{e(\varphi^*_W-V)}{kT_W} + \frac{A_{\mathrm{TW}}}{A_{\mathrm{TO}}}\exp\left[\frac{e(\varphi^*_W-V)}{kT_W} + \frac{e(V-\varphi_O)}{kT_O}\right]\right\}. \tag{3}$$

The estimate of V by formula (3) was made from the measured ratio $i_W = i_O = 1/4000$ at $T_W = 2200^\circ$ K and $T_O = 800^\circ$ K; $\varphi^*_W = 5.2$ V (^{8}); two values of φ_O were used: the thermionic work function $\varphi_{O1} =$

$= 5.9$–6.0 V, found from the delay curves (Fig. 2), and the effective work function with respect to the ionization of hard-to-ionize elements φ_{02}, determined by us from the ionization on the oxide of Bi atoms and equal to 6.8 V.

With a small error one may take the ratio $A^*_{\mathrm{TW}}/A_{\mathrm{TO}} = 1$. The value A^*_{TW} was also taken equal to unity, and the possible error due to this assumption is estimated below.

Equation (3) has a solution for φ_{01} when $\nu(T)_O/\nu(T)_W \geqslant 120$, and for φ_{02} when $\nu(T)_O/\nu(T)_W \geqslant 2$. The value $\nu(T)_O/\nu(T)_W$ is determined by different yields of the radical-formation reaction on W and on the oxide at different T, by different sticking coefficients of molecules to the emitters in the two cases, and also by different areas of the effectively emitting regions on tungsten and on the oxides. One finds $V \approx 5.9$ V if $\varphi_O = \varphi_{01}$, and $V \approx 6.7$ V if $\varphi_O = \varphi_{02}$. Since the distribution of regions with different work functions on the oxide is unknown, V may have a value within the limits $5.9 \leqslant V \leqslant 6.7$ V.

The ratio of the statistical sums A of the ionic and neutral states of atomic particles is a quantity of order unity. For polyatomic particles it may take values substantially different from 1. For $C_4H_{10}N$ the value of A is unknown. However, as follows from formula (3), V is only weakly sensitive to the value of A, and when A is changed by 4 orders of magnitude, from $A = 0.01$ to $A = 100$, the correction is $\Delta V = \mp 0.3$ V.

Thus, the radical $C_4H_{10}N$ apparently possesses one of the lowest adiabatic ionization potentials for particles of complex composition (^{9}).

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Note: Figure translations are in progress. See original paper for figures.