SPECIAL FEATURE
HISTORICAL

Secondary Processes in the Ion Source of a Mass Spectrometer (Presented by academician N. N. Semenov 27 VIII 1952)—reprinted from Report of the Soviet Academy of Sciences, *Volume LXXXVI,* -N5 (1952)

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We have investigated secondary processes in the gas phase ion source of a mass spectrometer in cases where individual saturated (methane, ethane, propane, butane) hydrocarbons and unsaturated (ethylene, propylene, isobutylene) hydrocarbons and also water are ionized.

It was shown that when the source pressure of the substance under investigation increases, the relative intensity of line 19 in the spectrum of water starts to increase. This means that the ion H_3O^+ appears in the spectrum of propylene when the relative intensity of the line 43 $(C_3H_7^+)$ increases, while in the spectrum of iso-butylene line 57 $(C_4H_9^+)$ increases. All these secondary ions have the same composition as the neutral molecules of the investigated substances but have one more proton.

In the case of ethylene, no such ions were found. In the case of saturated hydrocarbons where ions heavier by one proton than parent molecules would have a molecular formula $C_nH_{2n+3}^+$, we did not see those ions either, with the interesting exception of the lowest representative of this homologous series, methane; an increase in the source methane pressure results in increased formation of the CH_5^+ ion.

Experiments were carried out in the usual gas ion source[1] the anode of which was in the form of a $20 \times 10 \times 5$ mm chamber made of NiCr alloy. The side walls had 7×1 mm slits for introducing electrons from the filament and passing them through to the electron trap. The gas under investigation was introduced through a capillary entering the chamber through a 2 mm diameter orifice in the wall. Ions were extracted from the chamber by weak electric fields penetrating through the 10×1 mm slit in the direction perpendicular to the electron beam. Electron emission current was in the range of 0.1–1.0 mA in different experiments. Pressure was either measured by an ionization gauge, and in this case corrections were made for the flow resistance between the ionization region and pressure gauge,[a] or by a mercury gauge placed after the capillary. In the latter case the pressure in the source was deter-

mined using a calibration measurement made in advance.

Figure 1 demonstrates the linear dependence of the ratio η of protonated ion intensity to the intensity of the corresponding primary ions from water (3), propylene (1) and methane (2). These dependences were obtained at ionizing electron energy $U_e = 70$ eV. The y-axis presents the intensities of lines 19 *vs.* 18 in the case of water, 43 *vs.* 42 in the case of propylene and 17 *vs.* 16 in the case of methane. Intersection points of extrapolated straight lines with the y-axis correspond to the relative isotopic contents of the corresponding isotopic molecules (in propylene the normal $^{13}C_3H_6$ content is 3.3% in methane the normal content of $^{13}CH_4$ is 1.1%). Line 17 is always present in the spectra because of traces of
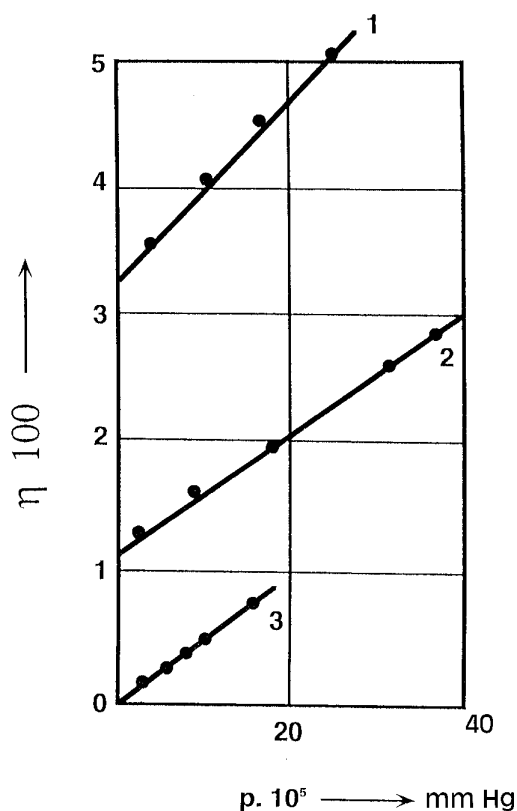

Figure 1.

water (OH^+ ions): in all cases the intensity of line 17 was corrected by subtracting the contribution of OH^+ ions from the measured intensity of line 17. This can be done with great accuracy, because line 18 (H_2O^+) was also measured and the intensity distribution of the lines in the water spectrum was carefully measured in advance. Figure 2 presents part of the spectrum of methane (left) at $p = 10^{-4}$ mmHg, $U_e = 60$ eV, and part of the water spectrum in the absence of methane (right, same U_e value). It demonstrates the intensity ratios of lines 17 and 18 and also the presence of the line 19, corresponding to H_3O^+ ions. Different hatch patterns on the line 17 in the left figure show the contributions of different ions to the peak intensity (a = OH^+, b = $^{13}CH_4^+$, c = $^{12}CH_5^+$).

The existence of H_3O^+ ions in solution is well known and it was indicated[2] that it can exist in an ion source too. The existence of this ion and also, as presented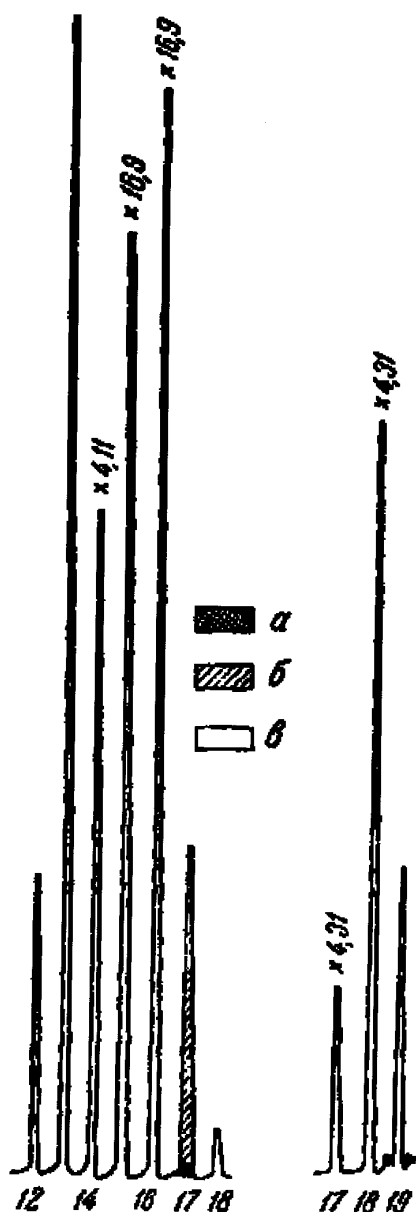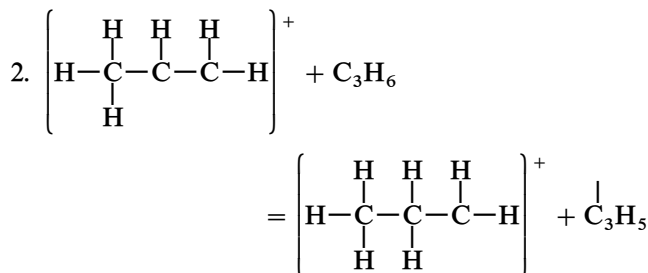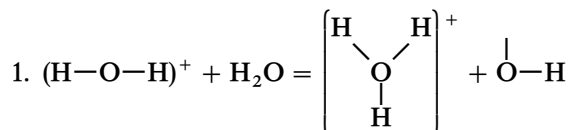 by us, $C_nH_{2n+1}^+$ ions in the case of olefins fall in the frame-work of conventional understanding of valence. The corresponding secondary processes can be presented taking into account the proportionality between η and pressure p, for instance in the following manner:

$$1.\ (H—O—H)^+ + H_2O = \begin{bmatrix} H \quad\quad H \\ \diagdown \diagup \\ O \\ | \\ H \end{bmatrix}^+ + \overset{|}{O}—H$$

$$2.\ \begin{bmatrix} H \quad H \quad H \\ | \quad | \quad | \\ H—C—C—C—H \\ | \\ H \end{bmatrix}^+ + C_3H_6$$

$$= \begin{bmatrix} H \quad H \quad H \\ | \quad | \quad | \\ H—C—C—C—H \\ | \quad | \\ H \quad H \end{bmatrix}^+ + \overset{|}{C}_3H_5$$

while the O—H bond in hydroxonium calls for participation of two $2p$ electrons from oxygen, which are not responsible for bonding in water.

The CH_5^+ ion story is different. We could call it the methonium ion. Because participation of the 1s electron of carbon in a bond is impossible, we are probably dealing here with a complex of the same kind as in the well known H_3^+ ion, where three protons are bound by two electrons.

To clarify the nature of the secondary process that lead to CH_5^+ ion formation, we studied the CH_4^+ and CH_5^+ ion current dependences on the ionizing electron energy. Initial parts of these curves are shown in Fig. 3,
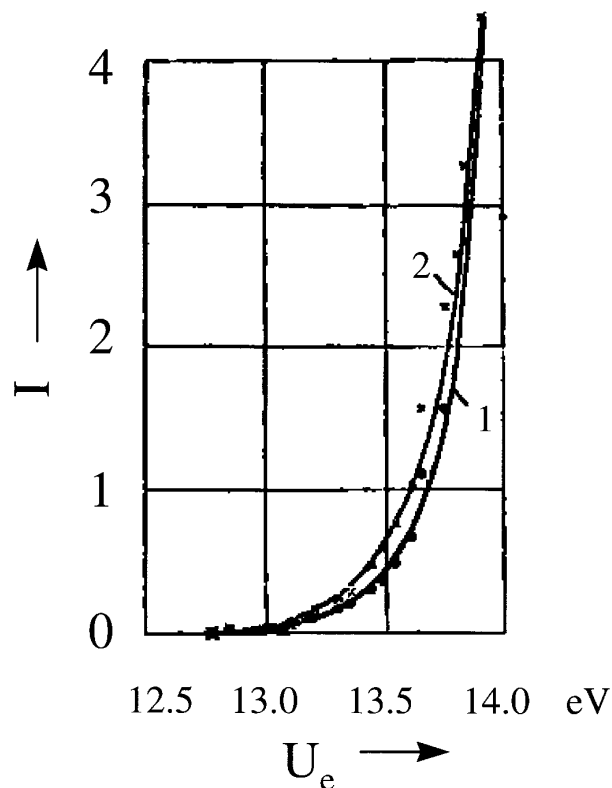

Figure 2.

Figure 3.

ᵃ With the $^{13}CH_4^+$ contribution subtracted.

where 1 and 2 depict the CH_4^+ and CH_5^+ (scaled up)[a] currents, respectively, and I is the ion current in arbitrary units. These data suggest that the potential needed for creation of CH_5^+ and the ionization potential of methane are the same within the experimental precision (± 0.05 V). The process follows:

3. $CH_4^+ + CH_4 = CH_5^+ + CH_3$
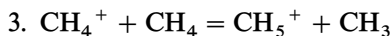
Unexpectedly in these terms, the η dependence, $\eta = f(U_e)$, drops abruptly with increasing U_e. Also, we found out that placing the ion source into the magnetic field collinear with the ionizing electron beam significantly increases η, especially in the region of small U_e.

Figure 4 shows the η vs. U_e dependence for methane (taking account of the $^{13}CH_4$ contribution) with (1) and without (2) the magnetic field. Both effects discussed above are thus illustrated. An analogous effect has been observed for isobutylene, but was not seen for propylene.

Despite these phenomena we do not think we have enough evidence for the existence of a mechanism for CH_5^+ creation different from process (3) as all the observed effects can be explained as follows. Let the CH_5^+ ion be created in process (3). Stationary-state conditions give

$$\frac{d(CH_5^+)}{dt} = k_3(CH_4^+)(CH_4) - k_2(CH_5^+) = 0 \quad (1)$$

where the parentheses represent concentrations, k_3 is the process (3) rate constant and k_2 is a 'rate constant' for the process in which the CH_5^+ ion leaves the area of
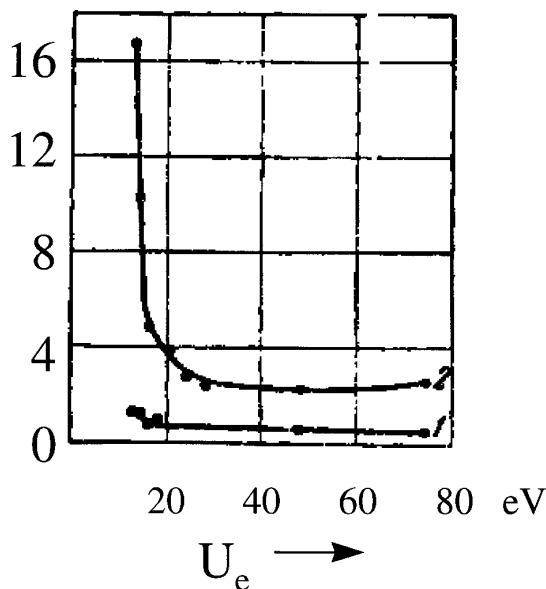
ionization, which depends on the initial velocity of the created CH_5^+ ions, repeller (extractor) field, ionization region size, trajectories of the ions in this region and space charge. Thus,

$$\eta \equiv \frac{(CH_5^+)}{(CH_4^+)} = \frac{k_3}{k_2}(CH_4) \quad (2)$$

The increase in η with the nature of the magnetic field applied obviously can be explained by a decrease in k_2 because of elongation and curving of the ion trajectories. The sudden jump of U_e in the vicinity of the ionization potential can be due to decreased compensation of the space charge and electron beam by positive ions. When the electron energy only slightly exceeds the work function, the later ion's yield is orders of magnitude smaller than in the maximum of the ionization function. The positive ion's slow down, which is caused by a rising negative space charge, must in turn lead to enhancement of the magnetic field effect. This has been seen experimentally. From this point of view, the absence of the magnetic field enhancement effect on η in case of propylene can be explained by the stong exoenergetic nature of process (1). The secondary ion's momentum right after its creation can be therefore so large that the magnetic field we were using, $H = 250$ Oe, may not be sufficient to elongate the ion trajectories significantly. On the other hand, the relative charge in velocity caused by the space charge is small.

The absence of the $C_2H_5^+$ ion line in the spectrum of C_2H_4 under high pressure can be explained by the fact that the process

$$C_2H_4 + C_2H_4^+ = C_2H_5^+ + C_2H_3$$
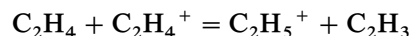
is endo-energetic by 0.9 eV.[3-6] Our understanding of the nature of the magnetic field effect on η in the case of similar observations for other systems, will provide a direct method for estimation of the heats of the secondary processes of interest. This method will require acting on η and thus on k_2 with magnetic fields of various intensities. We also studied the formation of H_3O^+ ions in case of ionization of CH_4 and H_2O mixtures. In particular we observed a linear correlation between the $(H_3O^+)/(H_2O^+)$ ratio and methane pressure, which suggests the process
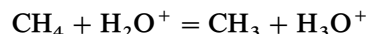
$$CH_4 + H_2O^+ = CH_3 + H_3O^+$$

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Figure 4.

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