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Mass Spectrometric Study of Positive Ion–Molecule Reactions in the C_3H_6 and Ar Mixtures Inside the High Pressure Ion Source

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Ion–molecule reactions have been measured for the propene–argon mixtures of different compositions using a quadrupole mass spectrometer with a high-pressure ion source. The concentration of propane in these mixtures ranged from 10% to 90% (at 10% increment). The following primary and secondary ions: CH_5^+ ($m/q = 17$), $C_2H_2^+$ ($m/q = 26$), $C_2H_3^+$ ($m/q = 27$), $C_2H_4^+$ ($m/q = 28$), $C_2H_5^+$ ($m/q = 29$), $C_3H_3^+/^{39}Ar^+$ ($m/q = 39$), $C_3H_4^+/^{40}Ar^+$ ($m/q = 40$), $C_3H_5^+$ ($m/q = 41$), $C_3H_6^+/^{42}Ar^+$ ($m/q = 42$), $C_3H_7^+$ ($m/q = 43$), $C_3H_8^+$ ($m/q = 44$), $C_4H_5^+$ ($m/q = 53$), $C_4H_6^+$ ($m/q = 54$), $C_4H_7^+$ ($m/q = 55$), $C_4H_8^+$ ($m/q = 56$), $C_4H_9^+$ ($m/q = 57$), $C_5H_5^+$ ($m/q = 65$), $C_5H_6^+$ ($m/q = 66$), $C_5H_7^+$ ($m/q = 67$), $C_5H_8^+$ ($m/q = 68$), $C_5H_9^+$ ($m/q = 69$), $C_5H_{10}^+$ ($m/q = 70$) were observed. Relative ion current intensities for primary and secondary ions are presented as a function of both total mixtures pressure and concentration of propene in the mixture. Primary ions were produced by electrons with the energy of 300 eV. The potential of repeller electrode V_R inside the ion source collision chamber was fixed at 5 V for all measurements. The total mixture pressure was changed from 0.7 to 26.6 Pa. Schemes of ion–molecule reactions were proposed.

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1. Introduction

Investigations of ion–molecule reactions in pure propene as well as the mixtures of propene with argon and various rare gases were carried out extensively by many scientists using different mass spectrometric techniques and methods.

The ion–molecule chemistry of propene has been studied extensively by the ion cyclotron resonance (ICR) [1–3] in a tandem mass spectrometer [4, 5] and by the photoionization-high-pressure mass spectrometry (HPMS) [6, 7]. Aquilanti et al. investigated ionic reactions in gaseous butenes [8]. Herod and Harrison used the mass spectrometer with a pulsed electron beam to study the reactions in propene [9]. The ion–molecule reactions in pure propene have been investigated by Peers using the 60° deflection mass spectrometer with the ion source pressures up to about 0.1 Torr [10]. The ion–molecule reactions of propene were investigated by several teams [11–16]. Initiation of the radical cation polymerization of propene has been observed following the selective ionization of benzene in the gas phase by the resonance two-photon ionization-high-pressure mass spectrometry (R2PIHPMS) and by the selected ion flow tube (SIFT) techniques [17]. Before examining the benzene–propene system, Pithawalla et al. investigated the ion chemistry of propene in Ar carrier gas under the high-pressure mass spectrometry (HPMS) conditions. The mixtures of 10% and 12.3% propene in Ar were ionized by nonresonant multiphoton ionization (MPI) using a KrF excimer laser at 248 nm [17]. A flowing-afterglow apparatus coupled with a low pressure chamber has been used to measure product ion distributions and rate constants in the charge-transfer reactions of Ar^+ with CH_4, C_2H_n ($n = 2, 4, 6$), and C_3H_n ($n = 6, 8$) at thermal energy [18]. The gas phase ion–molecule reaction of Ar^+ ions with propene have been studied in a mixture of 1% C_3H_6 + 99% Ar in the pressure range 1.33–39.99 Pa [19]. The measurements were performed using a quadrupole mass spectrometer with a high-pressure ion source. The fractional abundance (relative intensity of the ion currents) for the major ions: $C_2H_3^+$, $C_3H_3^+$, $C_3H_5^+$, $C_3H_7^+$, $C_4H_5^+$, $C_4H_7^+$ and argon ions have been determined as a function of gas pressure in the ion source and against the repeller electrode potential. In the case of ion–molecule reactions of Ar^+ with C_3H_6 Tsuji et al. [18] and Bederski [19] observed the following ion products: $C_2H_3^+$, $C_3H_3^+$, $C_3H_5^+$, $C_3H_7^+$, $C_4H_5^+$ and $C_4H_7^+$. In this paper authors measured ion–molecule reactions in the gas mixtures of propene with argon of various compositions where the additional CH_5^+, $C_2H_2^+$, $C_2H_4^+$, $C_2H_5^+$, $C_3H_4^+$, $C_3H_6^+$, $C_3H_8^+$, $C_4H_6^+$, $C_4H_8^+$, $C_4H_9^+$, $C_5H_5^+$, $C_5H_6^+$, $C_5H_7^+$, $C_5H_8^+$, $C_5H_9^+$ and $C_5H_{10}^+$ ions were observed. It is worth noting that the fractional abundance ($I_i/\sum I_i$) of $C_2H_3^+$, $C_3H_3^+$ and $C_3H_5^+$ ions recorded by Tsuji et al. was 26% ± 1%, 69% ± 2% and 5% ± 1%, respectively [18]. In our paper the fractional abundance ($I_i/\sum I_i$) of these ions, depending on the composition of the mixture, was 2%–13%, 6%–46% and 2%–14%, respectively.

The fundamental purpose of this work was to examine the ion–molecule reaction mechanisms by which positive

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ions are formed in the gas mixtures of propene with argon of various compositions.

The studies of ion–molecule reactions occurring in the mixtures of propene with argon are very important to understand elementary processes in the gas phase ion chemistry, and also to explain the role of such processes in ionosphere. Reconstruction of these reactions in the laboratory conditions and knowledge about reaction mechanisms can be very important to monitor and protect the Earth atmosphere [20].

2. Experimental

A quadrupole mass spectrometer with a special high--pressure ion source has been employed to study the ion–molecule reactions in the mixtures of propene with argon for the thermal ion energy [21, 22]. The primary positive ions were produced in the ionization chamber (of a high pressure ion source) by an electron beam. This beam was produced by the electrons emitted from a hot filament (rhenium thermocathode). The energy of the electrons can be changed from 10 eV to 500 eV. The stabilization of the electron beam current was achieved by maintaining a constant value of the total emission current of the electrons from the filament. A pure gas or a gaseous mixture has been introduced into the ion source collision chamber, where the gas pressure can be changed from 0.133 Pa to 133 Pa. The primary ions are swept toward the exit hole and then collide with neutral molecules producing secondary ions by the ion–molecule reactions. The ions formed in the ionization chamber are removed from the chamber by the electric field of the repeller electrode. The positive (relative to the ionization chamber) potential V_{R} is applied to the ion repeller electrode (opposite the ion exit hole). After passing through the ion exit hole, the ions are accelerated (by the voltage U_{a}) and focused in the beam by the system of electrostatic lenses and mass-analysed in a mass spectrometer. A Balzers 16--stage electron multiplier associated with a current amplifier is used to measure the registered ion currents. The mass spectrometer is equipped with a special computer interface for data collection and data analyses. Computer program permits work in three modes: analog, tabular and peak selector. For the ions of higher mass number m/q, a transmission loss (mass discrimination) must be taken into account [23]. In order to correct the errors resulting from ion discrimination effects in different regions of the mass spectrometer, the ion transmission coefficient on the ion path from the source to the collector of an electron multiplier (which could also work as a counter) was determined [24]. Ion–molecule reactions in the high-pressure mass spectrometers can take place in the beam of molecules outside the ion source. The studies of the ion intensity distributions in the effusion molecular beams were carried out in our Department [25, 26]. The mass spectrometer ion source parameters were optimized to reduce the number of ion–molecule reactions which can take place in the molecular beam outside the ion source.

Propene and argon used in the experiment, supplied by Merck's Lab were of the best available purity (99.0% and 99.5%, respectively). The mixtures of investigated gases, of well defined composition, were prepared in a separate leak system, and introduced to the ionization chamber of the ion source. The total gas pressure inside the collision chamber of the ion source was controlled by means of precise sapphire valve and measured by the MKS Baratron capacitance manometer which was calibrated in mTorr. The accuracy of pressure measurement was ±0.5 mTorr. Measurements were performed for different concentrations of propene in the mixture with argon (from 10% C_3H_6 + 90% Ar to 90% C_3H_6 + 10% Ar with 10% propene increment).

The quadrupole mass spectrometer is able to perform ion mass analyses in the range from 1 to 400 u.

The differential vacuum system was applied to separate the ion source and the analyzer regions evacuation. The high speed 2000 l/s diffusion pump to evacuate the ion source region and the 800 l/s diffusion pump for the analyzer evacuation was used. This system allows to increase the maximum pressure in the ion source, without disrupting the quadrupole ion filter working conditions.

All measurements were performed with the electron energy of 300 eV. Considering the fact that the measurements were performed at high pressure inside the ion source, energy of the electrons bombarding the gas should be higher than that corresponding to the maximum values of ionization cross-section for the investigated fragments. The multiple collisions of ionizing electrons with molecules are the reason for such selection of their energy. A large value of an electron beam energy assured good penetration of electrons at a high gas pressure in the ion source. The gas pressure inside the ion source collision chamber was varied from 0.7 to 26.6 Pa. The results of measurements were presented as dependences of the relative intensities of the observed ion currents from the total gas pressure of mixtures with different contents of C_3H_6 (at a fixed potential repeller $V_{\mathrm{R}} = 5$ V). In the author's opinion, the results of measurements presented in this paper are the first for such diverse mixture composition of C_3H_6 with Ar and for so high total gas pressures.

3. Results and discussion

In the present paper the authors made measurements of the ion–molecule in the propene–argon mixtures by means of quadrupole mass spectrometer with a high--pressure ion source [22]. Relative values of ion currents for the observed ions were determined as a function of the total gas pressure inside the collision chamber of the ion source for different mixture compositions. The measurements were performed for different concentrations of propene in the mixture with argon (from 10% C_3H_6 + 90% Ar to 90% C_3H_6 + 10% Ar with 10% increment). The recombination energy (RE) of Ar^+ ($^2P_{3/2}$) is 15.76 eV and Ar^+ ($^2P_{1/2}$) is 15.92 eV [27]. The ionization energy (IE) value of C_3H_6 is 13.19 ± 0.05 eV [28].

Primary ions were produced by the electrons with the energy of 300 eV and then they reacted with neutral gas molecules to form secondary and higher rate ions. The following primary and secondary ions: CH_5^+ ($m/q = 17$), $C_2H_2^+$ ($m/q = 26$), $C_2H_3^+$ ($m/q = 27$), $C_2H_4^+$ ($m/q = 28$), $C_2H_5^+$ ($m/q = 29$), $C_3H_3^+/^{39}Ar^+$ ($m/q = 39$), $C_3H_4^+/^{40}Ar^+$ ($m/q = 40$), $C_3H_5^+$ ($m/q = 41$), $C_3H_6^+/^{42}Ar^+$ ($m/q = 42$), $C_3H_7^+$ ($m/q = 43$), $C_3H_8^+$ ($m/q = 44$), $C_4H_5^+$ ($m/q = 53$), $C_4H_6^+$ ($m/q = 54$), $C_4H_7^+$ ($m/q = 55$), $C_4H_8^+$ ($m/q = 56$), $C_4H_9^+$ ($m/q = 57$), $C_5H_5^+$ ($m/q = 65$), $C_5H_6^+$ ($m/q = 66$), $C_5H_7^+$ ($m/q = 67$), $C_5H_8^+$ ($m/q = 68$), $C_5H_9^+$ ($m/q = 69$), $C_5H_{10}^+$ ($m/q = 70$) were observed.

In the mixtures of propene with argon, ion–molecule processes can take place according to the reaction scheme [3, 4, 9, 10, 14, 18, 19]:

$$Ar^+ + C_2H_2 \rightarrow C_2H_2^+ + Ar, \quad (1)$$

$$Ar^+ + C_3H_6 \rightarrow C_2H_3^+ + CH_3 + Ar, \quad (2)$$

$$Ar^+ + C_2H_4 \rightarrow C_2H_4^+ + Ar, \quad (3)$$

$$Ar^+ + C_3H_6 \rightarrow C_3H_3^+ + H_2 + H + Ar, \quad (4)$$

$$Ar^+ + C_3H_6 \rightarrow C_3H_4^+ + 2H + Ar, \quad (5)$$

$$C_3H_4^+ \rightarrow C_3H_3^+ + H, \quad (6)$$

$$Ar^+ + C_3H_6 \rightarrow C_3H_5^+ + H + Ar, \quad (7)$$

$$C_3H_5^+ \rightarrow C_3H_3^+ + H_2, \quad (8)$$

$$Ar^+ + C_3H_6 \rightarrow C_3H_6^+ + Ar, \quad (9)$$

$$C_3H_6 + e^- \rightarrow C_3H_6^+ + 2e^-, \quad (10)$$

$$C_3H_6^+ \rightarrow C_2H_3^+ + CH_3, \quad (11)$$

$$C_3H_6^+ \rightarrow C_3H_5^+ + H, \quad (12)$$

$$C_3H_6^+ \rightarrow C_3H_4^+ + H_2, \quad (13)$$

$$Ar + e^- \rightarrow Ar^+ + 2e^-, \quad (14)$$

$$C_3H_6^+ + C_3H_6 \rightarrow C_3H_4^+ + C_3H_8, \quad (15)$$

$$C_3H_6^+ + C_3H_6 \rightarrow C_3H_4^+ + C_3H_6 + H_2, \quad (16)$$

$$C_3H_6^+ + C_3H_6 \rightarrow C_3H_4^+ + C_3H_4 + 2H_2, \quad (17)$$

$$C_3H_6^+ + C_3H_6 \rightarrow C_3H_5^+ + C_3H_6 + H, \quad (18)$$

$$C_3H_6^+ + C_3H_6 \rightarrow C_3H_5^+ + C_3H_7, \quad (19)$$

$$C_2H_3^+ + C_3H_6 \rightarrow C_3H_7^+ + C_2H_2, \quad (20)$$

$$C_3H_6^+ + C_3H_6 \rightarrow C_3H_7^+ + C_3H_5, \quad (21)$$

$$C_3H_7^+ \rightarrow C_3H_4^+ + H_2 + H, \quad (22)$$

$$C_3H_7^+ \rightarrow C_3H_5^+ + H_2, \quad (23)$$

$$C_3H_3^+ + C_3H_6 \rightarrow C_4H_5^+ + C_2H_4, \quad (24)$$

$$C_3H_6^+ + C_3H_6 \rightarrow C_4H_6^+ + C_2H_6, \quad (25)$$

$$C_2H_3^+ + C_2H_3 \rightarrow C_4H_6^+, \quad (26)$$

$$C_3H_3^+ + C_3H_6 \rightarrow C_4H_7^+ + C_2H_2, \quad (27)$$

$$C_3H_6^+ + C_3H_6 \rightarrow C_4H_7^+ + C_2H_5, \quad (28)$$

$$C_3H_6^+ + C_3H_6 \rightarrow C_4H_8^+ + C_2H_4, \quad (29)$$

$$C_3H_5^+ + C_3H_6 \rightarrow C_4H_9^+ + C_2H_2, \quad (30)$$

$$C_4H_8^+ + C_3H_6 \rightarrow C_4H_9^+ + C_3H_5, \quad (31)$$

$$C_3H_2^+ + C_3H_6 \rightarrow C_5H_5^+ + CH_3, \quad (32)$$

$$C_3H_4^+ + C_3H_6 \rightarrow C_5H_7^+ + CH_3, \quad (33)$$

$$C_3H_6^+ + C_3H_6 \rightarrow C_5H_8^+ + CH_4, \quad (34)$$

$$C_3H_6^+ + C_3H_6 \rightarrow C_5H_9^+ + CH_3, \quad (35)$$

$$C_4H_8^+ + C_3H_6 \rightarrow C_5H_{10}^+ + C_2H_4, \quad (36)$$

$$C_3H_6^+ + C_3H_6 \rightarrow (C_6H_{12}^+)^*, \quad (37)$$

$$(C_6H_{12}^+)^* \rightarrow C_4H_7^+ + C_2H_5, \quad (38)$$

$$(C_6H_{12}^+)^* \rightarrow C_4H_8^+ + C_2H_4, \quad (39)$$

$$(C_6H_{12}^+)^* \rightarrow C_5H_7^+ + CH_5, \quad (40)$$

$$(C_6H_{12}^+)^* \rightarrow C_5H_9^+ + CH_3, \quad (41)$$

$$(C_6H_{12}^+)^* \rightarrow C_5H_{10}^+ + CH_2. \quad (42)$$

Figure 1 presents the relative intensity of the ion currents recorded as a function of gas pressure for the mixture of the composition of 10% C_3H_8 + 90% Ar, while Fig. 2 shows the same dependences for a mixture containing 90% C_3H_8 and 10% Ar.

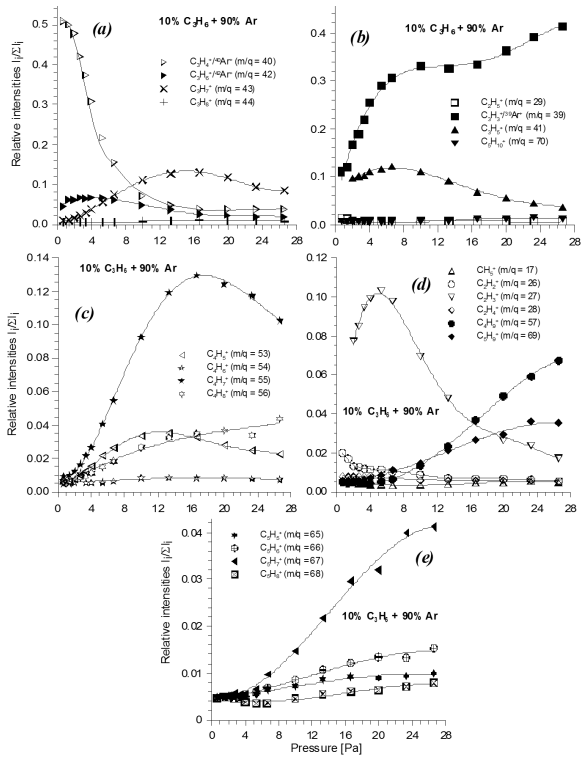

Fig. 1. Relative ion currents for: (a) $C_3H_4^+$ and/or $^{40}Ar^+$, $C_3H_6^+$ and/or $^{42}Ar^+$, $C_3H_7^+$ and $C_3H_8^+$, (b) $C_2H_5^+$, $C_3H_3^+$ and/or $^{39}Ar^+$, $C_3H_5^+$ and $C_5H_{10}^+$, (c) $C_4H_5^+$, $C_4H_6^+$, $C_4H_7^+$ and $C_4H_8^+$, (d) CH_5^+, $C_2H_2^+$, $C_2H_3^+$, $C_2H_4^+$, $C_4H_9^+$ and $C_5H_9^+$ and (e) $C_5H_5^+$, $C_5H_6^+$, $C_5H_7^+$ and $C_5H_8^+$ ions as a function of gas mixture pressure for 10% C_3H_6 + 90% Ar mixture. The repeller potential $V_R = 5$ V.

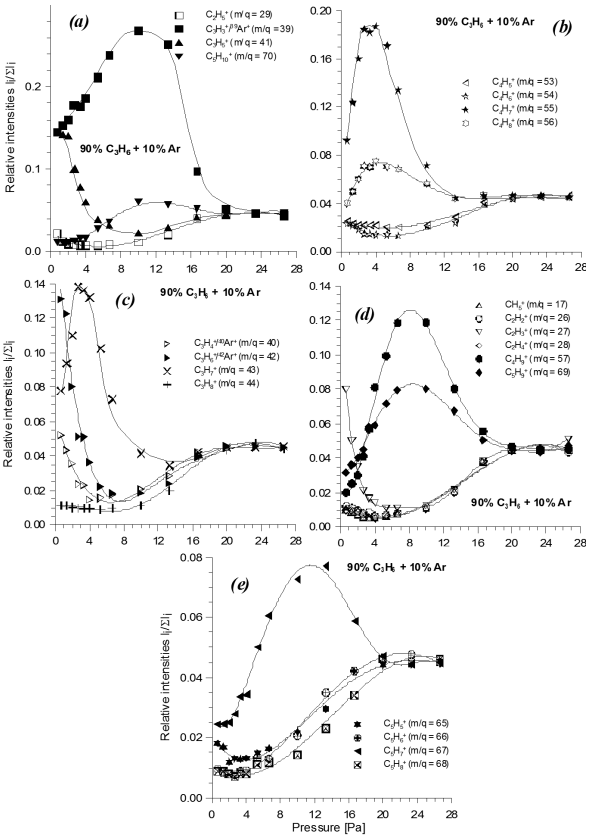

Fig. 2. Relative ion currents for: (a) $C_2H_5^+$, $C_3H_3^+$ and/or $^{39}Ar^+$, $C_3H_5^+$ and $C_5H_{10}^+$, (b) $C_4H_5^+$, $C_4H_6^+$, $C_4H_7^+$ and $C_4H_8^+$, (c) $C_3H_4^+$ and/or $^{40}Ar^+$, $C_3H_6^+$ and/or $^{42}Ar^+$, $C_3H_7^+$ and $C_3H_8^+$, (d) CH_5^+, $C_2H_2^+$, $C_2H_3^+$, $C_2H_4^+$, $C_4H_9^+$ and $C_5H_9^+$ and (e) $C_5H_5^+$, $C_5H_6^+$, $C_5H_7^+$ and $C_5H_8^+$ ions as a function of gas mixture pressure for 90% C_3H_6 + 10% Ar mixture. The repeller potential $V_R = 5$ V.

The main observed ions were $C_2H_3^+$, $C_3H_3^+$, $C_3H_4^+$, $C_3H_5^+$, $C_3H_6^+$, $C_3H_7^+$, $C_4H_7^+$ and $C_4H_9^+$. The relative intensities of CH_5^+, $C_2H_2^+$, $C_2H_4^+$, $C_2H_5^+$, $C_3H_8^+$, $C_4H_5^+$, $C_4H_6^+$, $C_5H_5^+$, $C_5H_6^+$, $C_5H_8^+$ and $C_5H_{10}^+$ ions observed during the experiment are very low and their contribution to the total ionization is lower than 4% and $C_4H_8^+$, $C_5H_7^+$ and $C_5H_9^+$ ions lower than 8%.

The relative $C_2H_3^+$ ion currents were observed in the experiment as the result of ion–molecule reactions (2) and (11). Only relative ion currents for $C_3H_3^+$ and $C_3H_4^+$ ions decrease with the increasing propane concentration in the mixture with argon. For all remaining observed ions relative ion currents increase as the propene concentration in the mixture with the argon increase. The $C_3H_3^+$ ions come from reactions (4), (6) and (8) while the $C_3H_4^+$ ions were produced as the result of reactions (5), (13), (15)–(17) and (22). The Ar^+ and $C_3H_4^+$ ions have the same mass to charge ratio. When the concentration of argon in the mixture decreases, relative ion currents for the $C_3H_4^+$ and/or Ar^+ ions clearly decrease, so one can assume that the Ar^+ ions dominate.

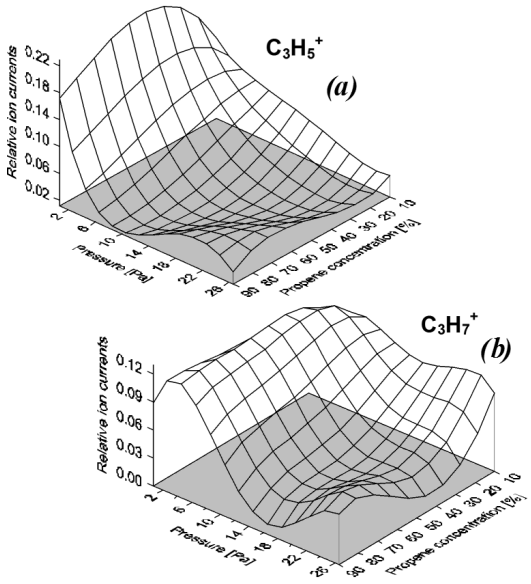

Fig. 3. Relative currents for secondary ions (a) $C_3H_5^+$ and (b) $C_3H_7^+$ as a function of propene concentration and total pressure of the propene–argon mixture. The repeller potential $V_R = 5$ V.

The relative $C_3H_5^+$ ion currents were observed as the result of ion–molecule reactions (7), (12), (18), (19) and (23). The $C_3H_6^+$ ions come from the charge-exchange reaction with argon (reaction (9)), mainly. The C_3H_6 molecules can also be ionized by electrons (reaction (10)). Thus formed $C_3H_6^+$ ions become fragmented giving a contribution to the relative intensities of $C_2H_3^+$, $C_3H_3^+$, $C_3H_4^+$ and $C_3H_5^+$ ion currents (reactions (6), (8), (11)–(13)). The ionization probability of C_3H_6 molecules by electrons increases with the increasing concentration of propene in the mixture. With the increasing mixture pressure in the ionization chamber of the ion source the number of collisions between the ions and neutral molecules increases, thus increasing the probability of the ion–molecule reactions occurrence. In consequence, the ions of the third order are produced in reactions (20), (21), (24), (27) and (30). Due to the transitional ion decay $(C_6H_{12}^+)^*$ formed in reactions (37), $C_4H_7^+$, $C_4H_8^+$, $C_5H_7^+$, $C_5H_9^+$, $C_5H_{10}^+$ ions were observed as the result of reactions (38)–(42).

Formation of $C_3H_7^+$ ions in reactions (20) and (21) was found. The relative ion currents observed for $C_3H_7^+$ and $C_4H_7^+$ have the maximum in the pressure range from 3 to 15 Pa (for $C_3H_7^+$ ions) and 4 to 17 Pa (for $C_4H_7^+$ ions), depending on the concentrations of propene in the mixtures, and then with the further gas pressure increase, drop of these ion current intensities was observed. A shift of this maximum in the direction of higher total mixture pressures can be observed as the concentration of propane in the mixture decreases. Relative ion currents for $C_3H_7^+$ and $C_4H_7^+$ grow with the increase of propene concentration in the mixtures with argon.

Figure 3a and b presents the three-dimensional plots of $C_3H_5^+$ and $C_3H_7^+$ relative ion currents as a function of propene concentration and the total pressure of the propene–argon mixture. The surfaces were obtained by approximation of the experimental results by polynomials of the third and fifth power.

4. Conclusions

Ion–molecule reactions were examined in a mixture of propene with argon for different concentrations of ingredients in a wide range of total mixture pressures.

Schemes of the reactions in which the observed ions may arise have been proposed by the authors. The main observed ions were $C_2H_3^+$, $C_3H_3^+$, $C_3H_4^+$, $C_3H_5^+$, $C_3H_6^+$, $C_3H_7^+$, $C_4H_7^+$ and $C_4H_9^+$. Additionally, in the contrast to Tsuji et al. [18] and Bederski [19], CH_5^+, $C_2H_2^+$, $C_2H_4^+$, $C_2H_5^+$, $C_3H_4^+$, $C_3H_6^+$, $C_3H_8^+$, $C_4H_6^+$, $C_4H_8^+$, $C_4H_9^+$, $C_5H_5^+$, $C_5H_6^+$, $C_5H_7^+$, $C_5H_8^+$, $C_5H_9^+$ and $C_5H_{10}^+$ ions were found. The fractional abundance $(I_i/\sum I_i)$ of the main recorded $C_2H_3^+$, $C_3H_3^+$ and $C_3H_5^+$ ions, depending on the composition of the mixture, was 2%–13%, 6%–46% and 2%–14%, respectively. In the paper by Tsuji et al. the fractional abundance $(I_i/\sum I_i)$ of these ions was $26\% \pm 1\%$, $69\% \pm 2\%$ and $5\% \pm 1\%$, respectively [18]. These differences may result from various spectrometric techniques and methods used in the studies. According to the authors knowledge, these are the first measurements carried out for such varied composition of mixtures and their total pressure.

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