

Study plasma-chemical processes of alkanes in atmospheric pressure corona discharge by ion mobility spectrometry-mass spectrometry (IMS-MS)

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In this work, we aim to study the plasma-chemical processes of alkanes (pentane, hexane, heptane, octane) in atmospheric pressure corona discharge. Detection of the neutral products will be carried out by ion mobility spectrometry (IMS) and mass spectrometry (MS) using the Atmospheric Pressure Chemical Ionization (APCI) method. In IMS, ions are separated based on both mass and size, allowing for the identification of various ions that may share the same mass (isomers). This capability enhances our ability to discern and characterize different forms of ions, providing valuable insights into the complex ionization products generated during the corona discharge of alkanes.

The processes of fragmentation alkanes and synthesis of new hydrocarbons will be studied in the corona discharge reactor. The analysis of saturated hydrocarbons (alkanes) remains a challenge using mass spectrometry due to their low acidity/basicity and the lack of ion acceptor functional groups in their structures [1, 2].

Sekimoto et al. studied direct analysis of alkanes in real time (DART)-mass spectrometry associated with corona discharge using He gas (corona-DART) [3]. The alkanes are ionized by Corona-DART as positive ions via hydride abstraction and oxidation. The product ions are $[M+O-3H]^+$ ($M+13$) and/or the analogous monohydrates $[M+2O-H]^+$ ($M+31$) which are primarily formed in the plasma jet with relatively high stability. Atmospheric pressure chemical ionization (APCI) of alkanes in air or in nitrogen with traces of oxygen is shown to yield regioselective oxidation, dehydrogenation, and fragmentation of alkanes [4]. Soft plasma ionization (SPI)-MS with a glow discharge ionization source was developed for ionization of alkanes [5]. They proposed a four-step reaction of alkane transformation with the resulting substance a protonated ketone ($[M+O-3H]^+$) [5].

A standalone IMS and an IMS-time-of-flight mass spectrometer (IMS-TOFMS) used in this study were homemade instruments constructed at the Department of Experimental Physics of Comenius University [6].

In this work, we used atmospheric pressure corona discharge for the ionization of saturated hydrocarbons. The experimental setup for ionization and transforming alkanes to IMS is shown in Fig.1. It consists of the external corona discharge, carrier gas, syringe pump for injecting sample, and IMS as a detector. Alkanes are ionized by using ext. CD system and the neutral products are transferred to IMS to be ionized and detected. The experiment is done at low and high current ($3\mu\text{A}$ and $10\mu\text{A}$) of ext. CD in different type of gas: Air, nitrogen (N_2), and oxygen (O_2).

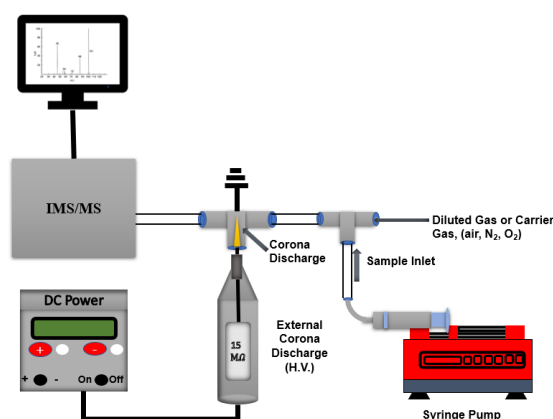


Figure 1: Schematic view of the external Ion Source (Corona Discharge) for ionization of alkanes.

Figures 2a and b show ion mobility and mass spectra of n-pentane (pent-72 g/mol) in positive polarity of ext. CD in air atmosphere. The main products ions are detected as $[\text{pent}+\text{O}-3\text{H}]^+$ (m/z 85, $[\text{C}_5\text{H}_{10}\text{O}_2-\text{OH}]^+$, $[\text{pent}+\text{O}-\text{H}]^+$ (m/z 87, 2-pentanone and 3-pentanone) and $[\text{pent}+\text{O}-\text{H}]^+\text{H}_2\text{O}$ (m/z 105), originating from hydride abstraction and oxidation reactions.

The experiment was repeated in O_2 and N_2 atmosphere as carrier gas into ext.CD system. Oxygen is known to produce ozone in corona discharges [7] and is likely responsible for the oxidation of saturated Hydrocarbons [8]. Fig. 2 (c) shows the comparison of IMS spectra with different carrier gasses (Air, N_2 and O_2). The mass spectra in Fig.2 show that the ion mobility peak at drift times of 5.3 ms (m/z 145) and 5.8 ms (m/z 173) are probably related to a proton-bound dimer $[\text{2Pentane}]\text{H}^+$ and $[\text{2Pentanone}]\text{H}^+$ respectively in O_2 atmosphere.

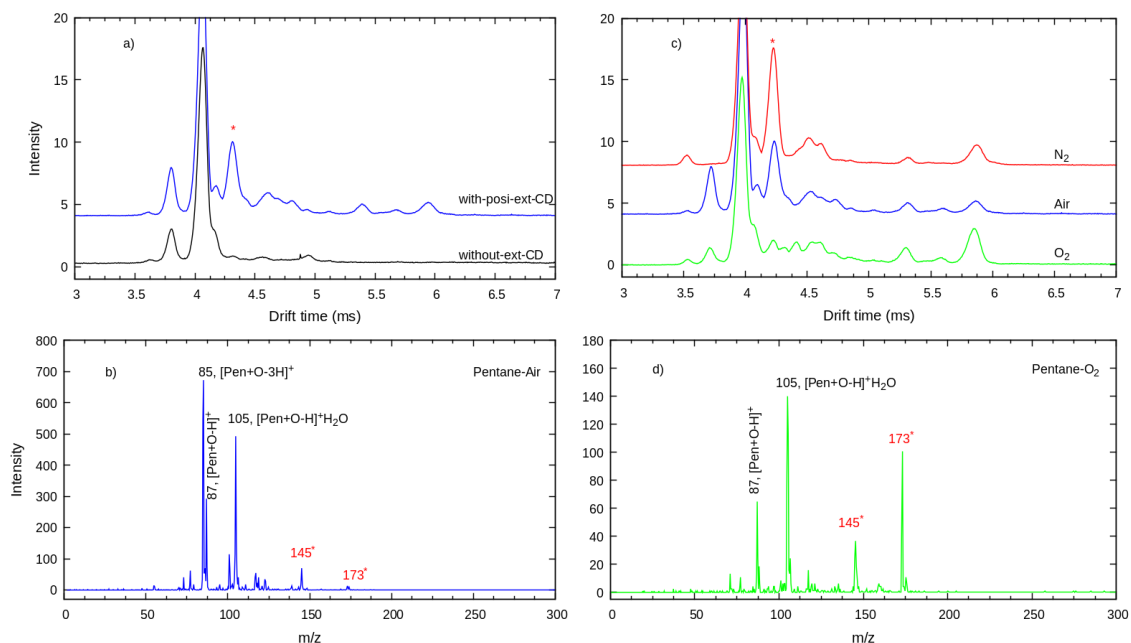


Figure 2: a) Ion mobility spectra of 30 ppm-pentane with and without ext.CD in positive polarity, b) Mass spectra of pentane in positive ext.CD, c) Comparison of ion mobility spectra of 30 ppm-pentane in O_2 , N_2 and Air in positive polarity of ext.CD, d) Mass spectra of pentane in O_2 .

Keywords: Saturated hydrocarbons, Mass spectrometry, Corona discharge, Oxidation reaction, ion formation

Acknowledgment

The present studies were supported by the Slovak Grant Agency for Science VEGA Nr. 1/0489/21, Slovak Research and Development Agency under project Nr. APVV-19-0386 and Nr. APVV-22-0133.

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