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High Pressure Ion Source for the Investigation of Ion-Molecule Reactions

INTRODUCTION

The high pressure ion source presented in this paper was employed to pursue the investigation of ion-molecule reactions at pressures within the range 10^{-3}–1 Tr and in a wide range of temperatures up to 500 K. The electron energy was varied from 70 to 600 eV. Hence it can be seen that the ion source described here is a relatively versatile one.

As is well known, this type of source, unlike conventional ion sources requires some particular additional conditions to be met [3].

The collision chamber, due to the high pressure inside, should be adequately gastight (the size of the ion exit and electron entrance apertures should be as small as possible, not exceeding 0.2–0.3 mm^2). The electron current should be stabilized according to the current signal reaching the first electrode 3 below the filament. It is necessary to use a differential pumping system (pump capacity ca 2000 l/s from the source side) so that the pressure outside the source is not higher than 10^{-4}–10^{-5} Tr. As the collision chamber is at a high potential relative to the mass spectrometer with a sector magnetic field, care should be taken to avoid a discharge in the gas conduit.

Numerous reports on high pressure ion source can be found in literature [4–11]. The authors presented in this paper construction of ion source, characteristics of source and study of charge transfer ion-molecule reactions in 2-pentene/carbon monoxide mixture as a function of pressure (in collision chamber) in the range from 10 to 200 mTr.

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EXPERIMENTAL

The high pressure ion source was adopted to the mass spectrometer with 60° sector magnetic field. A new source can in principle be applied to most commercial mass spectrometers to study ion-molecule reactions. It is a closed type source (in consideration of the high pressure in the collision chamber) with an electron beam to ionize the gas. Thus, the source block has only two slits: the inlet one for the electron beam (size: 2.00×0.15 mm) and the outlet one for ions (size: 1.022×0.175 mm). A schematic diagram of the ion source is shown in Fig. 1.

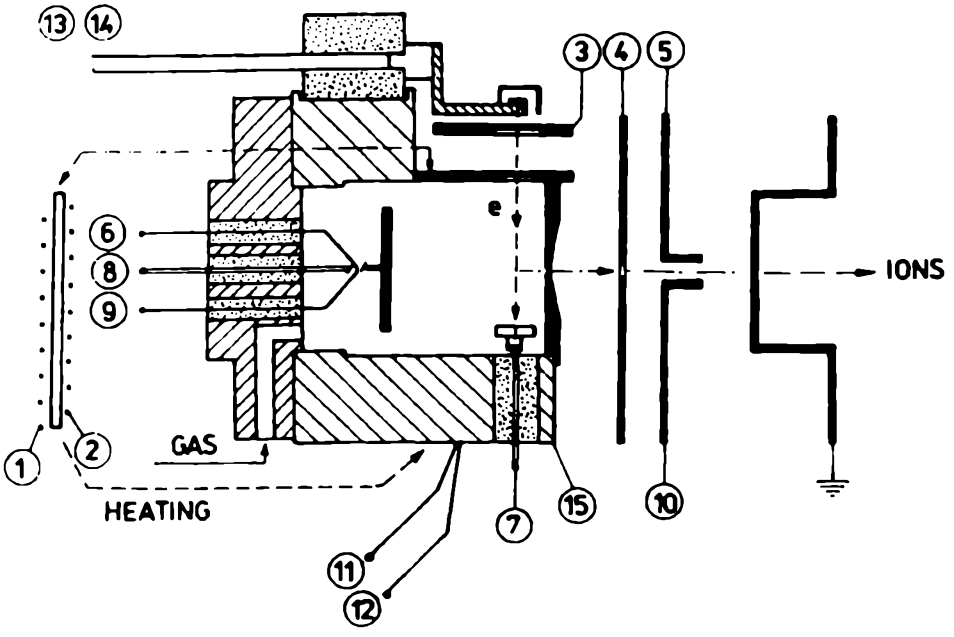

Fig. 1. Longitudinal section of the high pressure ion source

The electron beam emitted by the filament 13, 14 enters the collision chamber region and ionizes a gas or gas mixture in there. On its way the beam is shaped by an electrode 3 between the filament and the chamber. With gas pressures in the collision chamber ranging from 10^{-4} to 10^{-5} Tr it can be assumed that the whole of the electron current reaches the electron trap 7 and thus a measurement of its intensity is reasonable.

It is different at higher pressures from 10^{-2} to 1 Tr when — due to a high concentration of molecules in the collision chamber — the electron current reaching the trap is only a part of the electron current entering the chamber through the inlet slit. Thus, at higher pressures the electron trap is not so important any more. The electron current is stabilized by keeping a constant emission current at electrode 3.

The gas is metered out into the source from a gas inlet system through an orifice in the wall of the source block (on its left-hand side) below the repeller 8. The ion source can be heated to the temperature of ca 500 K owing to two heating coils located in the source block in parallel to the electron beam. Thermocouple 6, 9 measures the gas temperature inside the source, while thermocouple 11, 12 enables a measurement of the source block temperature. The ions generated in the collision chamber are extracted by an extracting electrode 4. Then, the ion beam goes between deflecting electrodes 5, 10 and gets to the inlet slit of the mass spectrometer. A schematic diagram of the ion source, mass analyser and detection system is shown in Fig. 2.

The spectrometer was entirely built at the Chemistry Institute of Laval University, Québec, Canada.

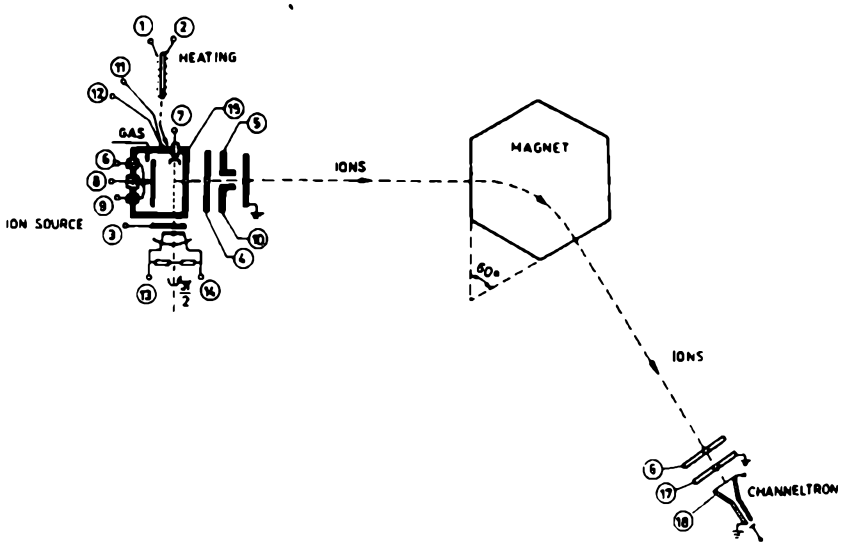

Fig. 2. High pressure mass spectrometer diagram

A very uniform magnetic field (12 kGs max.) is generated by an electromagnet (the one from NMR was used, working under saturation conditions) with poletips shaped like a hexagon inscribed into a circle. A channeltron 18 of ca 10^7 current amplification was adopted as a detection system. The vacuum system of the mass spectrometer is of a differential type and very high capacity diffusion pump of 2000 l/s pumping rate was used from the ion source side due to the high gas pressure in the collision chamber. The system metering out gas to the ion source can be heated to the temperature of ca 385 K.

As for the operating conditions of the ion source, the source block is at 2–3 kV potential relative to ground. The filament 13, 14 is kept at potential from −70 to −600 V relative to the collision chamber. The rhenium filament is fed with ca 4.0 A current. The electron trap 7 is at some low positive potential which considerably

improves the electron beam focusing, but then the electric field entering the collision chamber gets distorted. The repeller 8 is also at a low potential relative to the collision chamber. In practice, however, when investigating ion-molecule reactions, both the electron trap and the repeller had their potential equal to that of the collision chamber.

RESULTS AND DISCUSSION

Operating conditions of the high pressure ion source make it necessary to employ very efficient pumping system from the source side. In order to determine an operating pressure range for the source, a characteristic has been plotted as in Fig. 3.

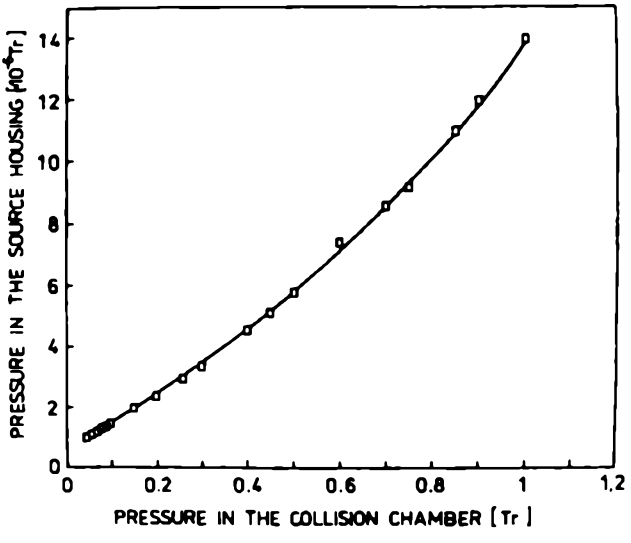

Fig. 3. Pressure in the source housing vs pressure in the collision chamber

As can be seen, when the air pressure in the collision chamber is 0.8 Tr, the pressure outside drops to 10^{-5} Tr. Thus, the maximum gas pressure in the collision chamber should not exceed 1 Tr to keep the source operative (in consideration of vacuum in the source region). When the gas was not metered out, the pressure in the source region was about 10^{-7} Tr.

The gas in the collision chamber was ionized by an electron beam produced by the rhenium filament. Fig. 4 shows the electron current intensity detected at the trap and the emission current intensity measured at electrode 3 as a function of the filament current. The relationship was plotted assuming 500 eV electron energy and 10^{-5} Tr air pressure in the collision chamber.

A characteristics family has been plotted showing the electron current intensity detected at the electron trap as a function of electron energies (Fig. 5), assuming various trap potentials and 0.1 Tr air pressure in the collision chamber.

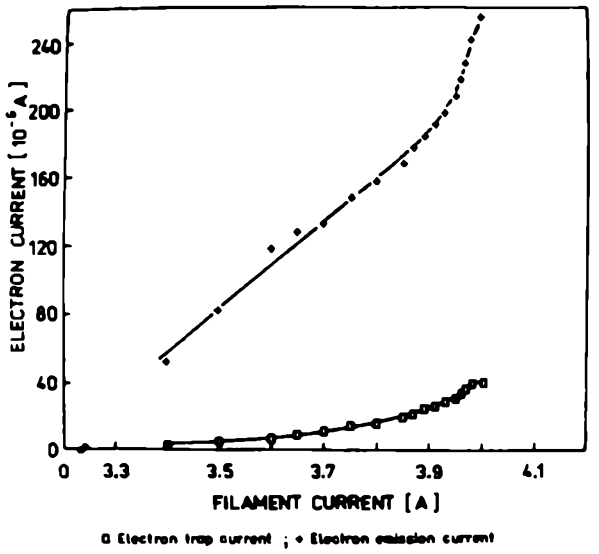

Fig. 4. Electron emission current and electron trap current vs filament current intensity

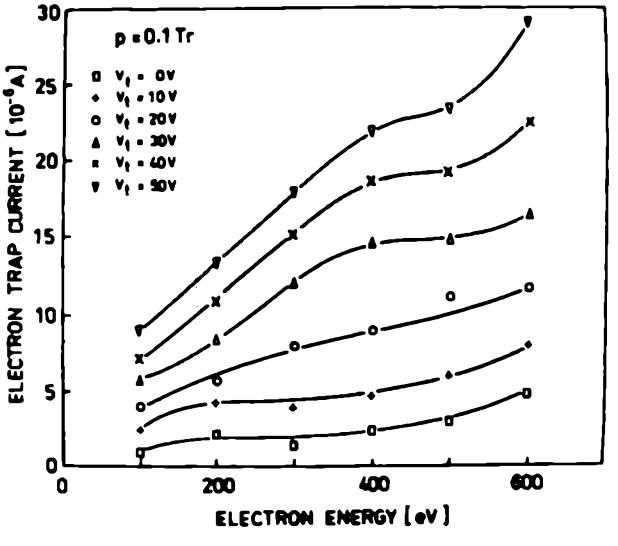

Fig. 5. Electron trap current vs electron energy

The same pressure was employed when measuring variations of the electron trap current as a function of the voltage applied between the trap and the collision chamber (Fig. 6), assuming various electron energies.

Having plotted the characteristics enabling further operating parameters of the high pressure ion source to be established a scaling procedure was started for the mass spectrometer (i.e. assignment of particular m/e values to the detected peaks), using PFK as a marker.

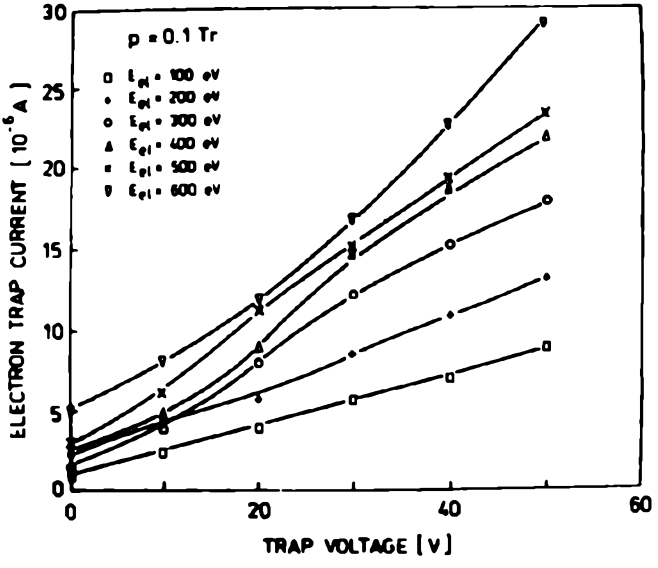

Fig. 6. Electron trap current vs trap voltage

Fig. 7 shows a 2-pentene mass spectrum, assuming 500 eV electron energy, 2.5 kV ion energy, 0.09 Tr pressure and 325 K temperature.

Peaks of CH_3^+, $C_2H_3^+$, $C_3H_3^+$, $C_4H_7^+$ and $C_5H_{10}^+$ can be clearly seen.

A charge transfer mass spectrum of ion-molecule reactions was determined for a 2-pentene / carbon monoxide mixture (a concentration ratio of the sample gas to the reagent gas was 1:250). As it is well known, the charge transfer reaction can be written as:

$$X^{+\cdot} + M \rightarrow M^{+\cdot} + X.$$

For the reaction to take place, the recombination energy (RE) of the reacting ion should be higher than the ionization energy (IE) of the neutral molecule M. The recombination energy of the ion $X^{+\cdot}$ is defined as extothermicity of the reaction [2]:

$$X^{+\cdot} + e \rightarrow XREX^{+\cdot} + -\Delta H.$$

The recombination energy of CO is 14.0 eV while the ionization energy of C_5H_{10} is 9.5 eV.

Fig. 8 gives a charge-transfer mass spectrum of 2-pentene, assuming 0.18 Tr pressure, 300 eV electron energy, 2.5 kV ion energy and 325 K temperature.

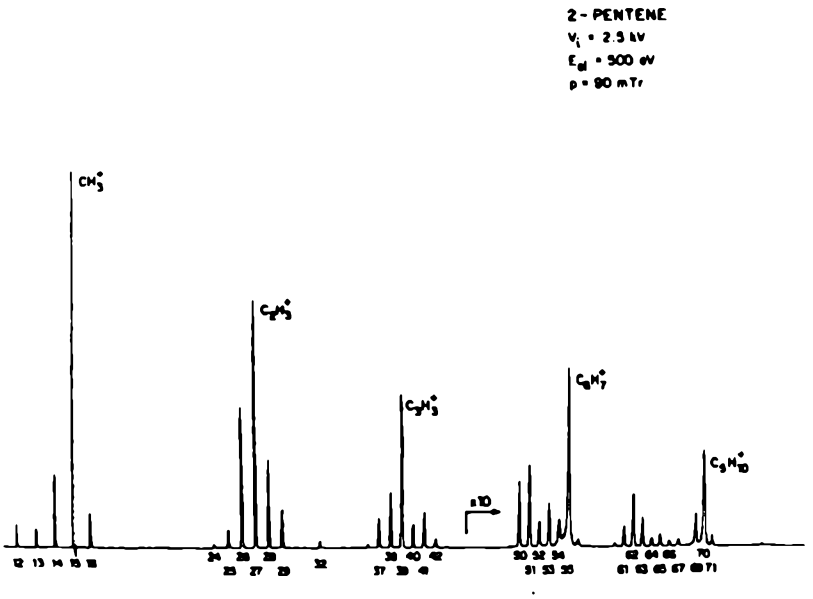

Fig. 7. 2-pentene mass spectrum for m/e ranging from 10 to 100 amu

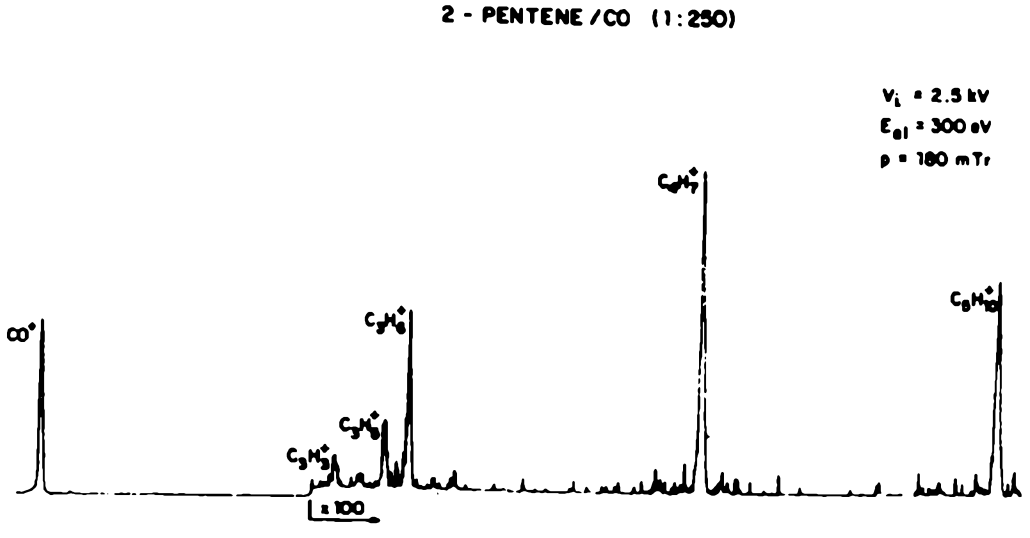

Fig. 8. 2-pentene charge-transfer mass spectrum

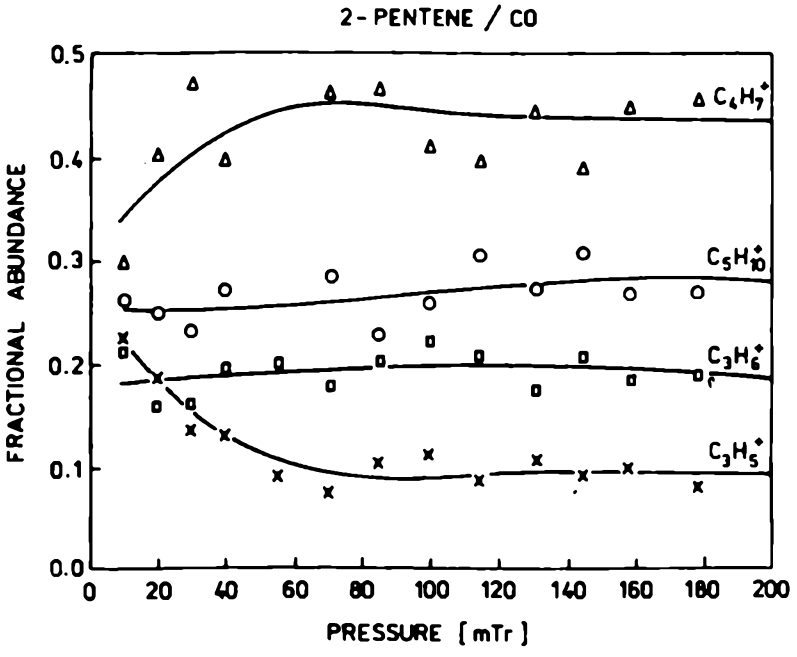

Fig. 9. Fractional abundance of the predominating ions in 2-pentene vs collision chamber pressure

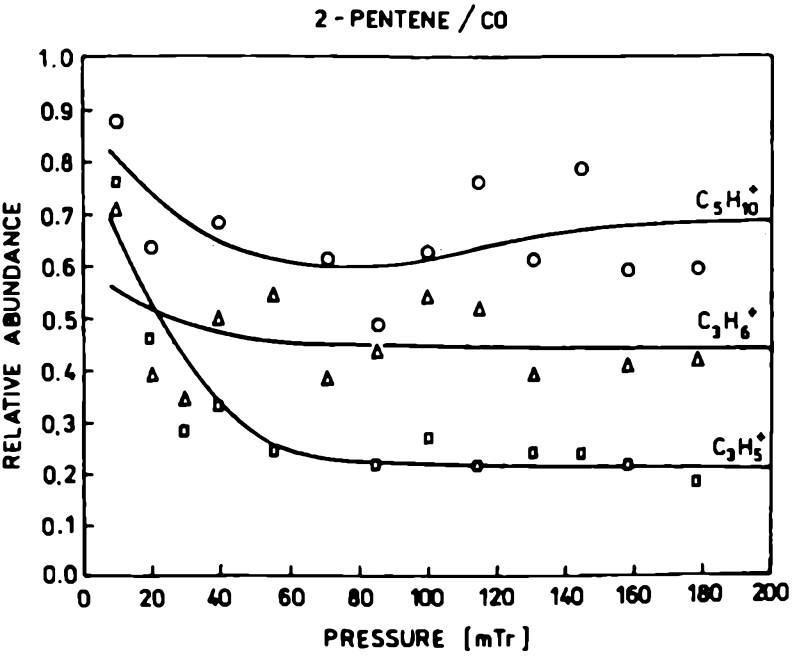

Fig. 10. Relative abundance of $C_5H_{10}^+/C_4H_7^+$, $C_3H_6^+/C_4H_7^+$ and $C_3H_5^+/C_4H_7^+$ in 2-pentene vs collision chamber pressure

The spectrum clearly shows peaks of mass numbers m/e=41, 42, 55 and 70. Ion current intensities corresponding to those peaks are lower by two orders of magnitude than that corresponding to CO^+ ions. The reaction pattern can be stated as follows [12]:

$$CO^{+\cdot} + C_5H_{10} \rightarrow C_5H_{10}^{+\cdot} + CO$$
$$C_5H_{10}^{+\cdot} \rightarrow C_4H_7^+ + CH_3$$
$$C_5H_{10}^{+\cdot} \rightarrow C_3H_6^{+\cdot} + C_2H_4$$
$$C_5H_{10}^{+\cdot} \rightarrow C_3H_5^+ + C_2H_5$$

Fig. 9 shows a fractional abundance of predominant ions generated in charge transfer ion-molecule reactions of 2-pentene as a function of the collision chamber pressure up to 0.2 Tr. As shown in Fig. 9, the fragmentary $C_4H_7^+$ ions predominate in ion-molecule reactions and they show some slight increase in 10–70 mTr pressure range. $C_3H_5^+$ ions are least abundant and they tend to drop in number with an increase of pressure. Relative abundance of $C_5H_{10}^{+\cdot}$ ions and also $C_3H_6^{+\cdot}$ and $C_3H_5^+$ ions show independence from the pressure above 100 mTr (Fig. 10).

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