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High Pressure Mass Spectrometer for the Investigation of Ion-molecule Reactions in Gases

Dedicated to Professor
Mieczysław Subotowicz
on occasion of his 65-th
birthday and 45-th years
of scientific work

INTRODUCTION

During the last twenty years a dynamic growth of new applications of mass spectrometry has been observed. Among these applications mass spectrometry methods used for studying ion-molecular reactions grasp an extensive significance. For these reactions to be observable, the primary ions /generated for example when bombarding the gas with electrons/ should encounter suitable conditions. It can be attained in two ways: by increasing the time the primary ions stay in the source /ion trapping/ at a relatively low gas pressure of the order 10^{-6} Tr [1-3] or by significantly increasing the gas pressure in the ion source [4-12]. Both these methods

lead to an increase in the number of primary ion collisions with neutral molecules, and consequently a growth in the probability of occurrence of the reaction is observed.

The authors constructed a high-pressure mass spectrometer for studying ion-molecular reactions under high-pressure conditions in the ion source.

EXPERIMENTAL

The mass spectrometer consists of a high-pressure ion source, a quadrupole mass filter and an ion detection system /type CU-03, made in USSR/. The schematic diagram of the spectrometer is presented in Fig.1, while the longitudinal section of the ion source is shown in Fig.2.

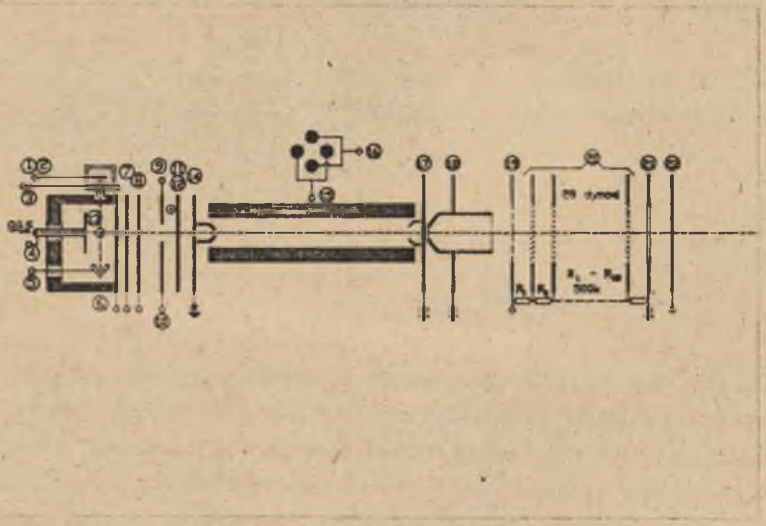

Fig.1. Schematic diagram of the high-pressure mass spectrometer.
1,2-filament, 3-forming electrode, 4-repeller, 5-electron collector, 6-collision chamber, 7-extracting electrode, 8-accelerating electrode, 9,10- deflecting electrodes /vertical/, 11,12-deflecting electrodes /horizontal/, 13-joint for MKS Baratron manometer, 14-outlet electrode, 15,16-rods of quadrupole mass analyser, 17,18-conic cylindrical electro-

des, 19-electron multiplier grid, 20-multiplier dynodes, 21-ring, 22-electron collector.

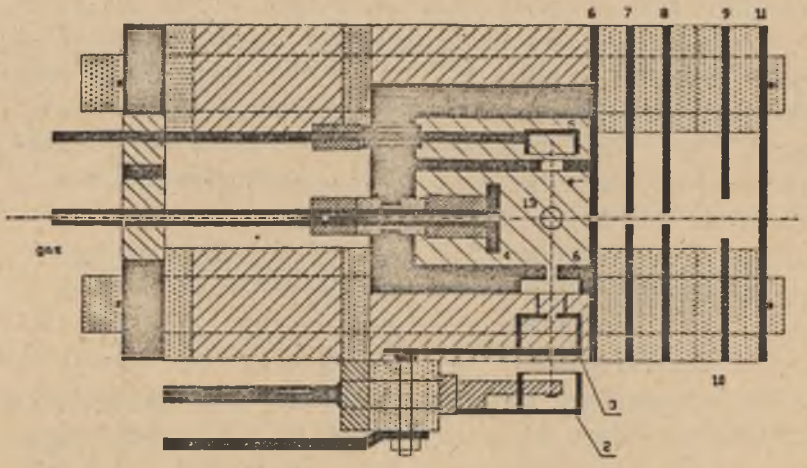

Fig.2. Longitudinal section of the ion source.

The electrons emitted from the tungsten or rhenium filament /1,2/ shielded by a penthouse, are accelerated towards the collision chamber /6/ by suitable potential difference determining electron energies. The electrons are then formed into a beam by forming electrode /3/ maintained at a positive potential relative to the filament. Changing the potential of this electrode one can optimize the electron focusing conditions. The electron energy is varied from 10 to 500 eV. The electron current is measured in the electron collector circuit /5/ featuring a positive polarization relative to the collision chamber. The collector potential can be varied within tens of volts in order to obtain saturation of the electron current. The collector is electrostatically shielded from the area of the collision chamber. Stabilization of the electron current accounting for the gas ionization can be provided for by maintaining a constant emission current / of several mA / in the circuit including the cathode and the forming electrode / 3 /.

A gas or a gas mixture is fed to the collision chamber through a capillary tube making a part of the repeller / 4 /. Pressure in the ionization space is measured by means of an MKS Baratron differential pressure gauge connected to the collision chamber at one end / joint /13// and to a vacuum system of a reference pressure of some 10^{-6} Tr at the other. The pressure in the ionization space/ collision chamber / can be changed from 10^{-3} to 1 Tr. For those high pressures to be obtainable, diameters of the inlet port for the electrons and the outlet port for the ions / in the ion source collision chamber housing / can not be greater then 0.5 mm. The ions generated by the electron beam on its way can be forced out by the repeller / 4/ the potential of which relative to the collision chamber can vary from 0 to 50 V. On their way towards the outlet, the primary ions interact with neutral gas molecules. The resulting secondary ions accompanied by the primary ones are extracted and formed into a beam by electrodes / 7,8 /of suitable selected potentials. Electrodes / 9-12 / form a deflecting system allowing the beam to be precisely focused on the inlet port /14/ of the quadrupole mass filter. The mass filter head and the ion source were manufactured in the Institute of Physics of Maria Curie-Sklodowska University in Lublin.

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

The ion detection system is provided with an electron multiplier which can also serve for an ion counter. Ion currents can also be measured directly by means of Faraday cup tape collector.

Due to the high pressure in the collision chamber of the ion source, a differential pumping system of 2000 l/s /from the source side / and 800 l/s / from the analyser and detector side / was used. Reduction of the pressure occures at 0.5 mm dia. orifice separating the areas of source and the analyser.

RESULTS

The authors carried out test measurements for ion-molecular reaction encountered in methane [13-19]. With low methane

pressures of 10^{-5} - 10^{-6} Tr generation of CH_4^+ ions and ionized dissociation product: CH_3^+, CH_2^+, CH^+, C^+, H_2^+ and H^+ in the collision chamber of the ion source can be observed. With high pressures of methane in the source, beginning from several tens mTr, secondary reactions can be observed [16] :

$$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3 \qquad /1/$$

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2 \qquad /2/$$

$$CH_2^+ + CH_4 \rightarrow \begin{cases} C_2H_4^+ + H_2 & /3/ \\ C_2H_3^+ + H_2 + H & /4/ \end{cases}$$

$$CH^+ + CH_4 \rightarrow C_2H_2^+ + H_2 + H \qquad /5/$$

Fig.3 illustrate relative ion currents vs. methane pressure in the collision chamber.

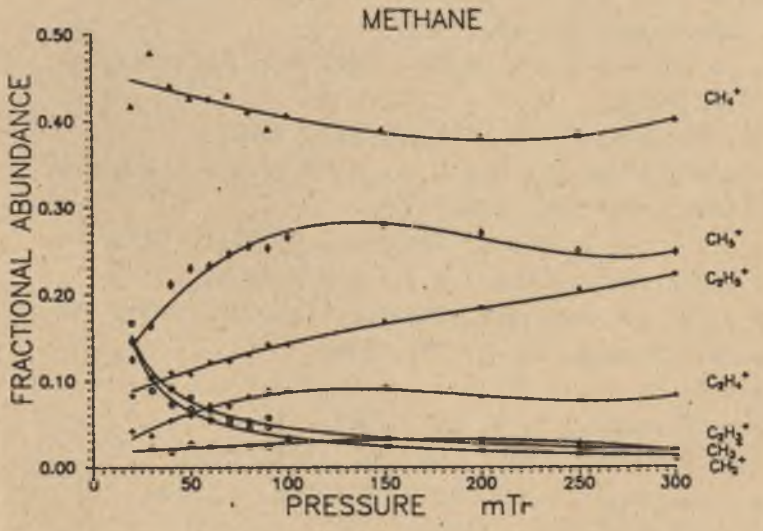

Fig. 3 Relative values of ion currents as a function of methane pressure /Electron energy 500 eV/.

It can be seen that the secondary ions CH_5^+ , $C_2H_5^+$, $C_2H_4^+$, $C_2H_3^+$ and also very small amount of $C_2H_2^+$ / not presented in Fig. 3 / anticipated by the reaction

/1-5/ were observed [13-19] . Dominant secondary ions are CH_5^+ and $C_2H_5^+$.

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