ASSOCIATION IONIZATION IN REACTIONS OF EXCITED NOBLE GAS ATOMS WITH NO, CH_3OH AND C_6H_6 MOLECULES

S.E. Kupriyanov, A.A. Perov, A.N. Stepanov
L.Ya. Karpov Institute of Physical Chemistry, Moscow, USSR.

ABSTRACT

Association ionization in binary mixtures of noble gases with ^{15}NO, ^{14}NO, CH_3OH and C_6H_6 molecules has been investigated using a mass spectrometer with a two-chamber ion source. Formation of complex ions $ArNO^+$, $KrNO^+$, $XeNO^+$, $ArCH_3OH^+$ and $ArC_6H_6^+$ in single collisions of metastable Ar, Kr and Xe atoms with the molecules has been detected.

1. INTRODUCTION

Excited noble gas atoms are known to result in association ionization on collisions with atoms and molecules forming different complex ions such as He_2^+, Ar_2^+, $HeAr^+$ (1), $ArC_2H_2^+$, $ArC_2H_4^+$ (2), ArH_2S^+, KrH_2S^+ (3) and other diatomic and polyatomic ions (4). The purpose of the present work was to investigate associative ionization proceeding in binary mixtures of noble gases (Ar, Kr, Xe) with nitrogen oxide, methyl alcohol and benzene molecules and involving metastable and long-lived highly excited atoms.

2. EXPERIMENTAL

The study was carried out with a "Varian MAT-731" mass spectrometer using a specifically designed two-chamber ion source allowing separation of excitation region from the region where the excited atoms react. The source schematic is shown in Fig.1 Noble gas was admitted to the first chamber (I) through a multichannel capillary array (MC). Metastable and highly excited states of noble gas atoms were excited by electron impact of variable energy, the ions and electrons formed were eliminated from the beam by a transverse electric field created by two plates (P1,P2) located between the excitation chamber and the collision one. Thus, only neutral atoms in long-lived metastable and high-Rydberg states with lifetimes 10^{-5} s could enter the second chamber (the distance between the chambers was of 2 cm). Molecular gas target (^{14}NO, ^{15}NO, CH_3OH and C_6H_6) was inlet to the second chamber transversely to the excited noble gas atom beam. Partial pressures of the components were less than 5×10^{-5} Torr. The electron emission current was 50÷200 μA, the exciting electron energy was varied within the range 8÷50 eV. The electric voltage on the deflecting plates P1,P2 was ±20 V. Ions formed in collisions of excited atoms and unexcited molecules were extracted, accelerated and analyzed mass

spectrometrically.

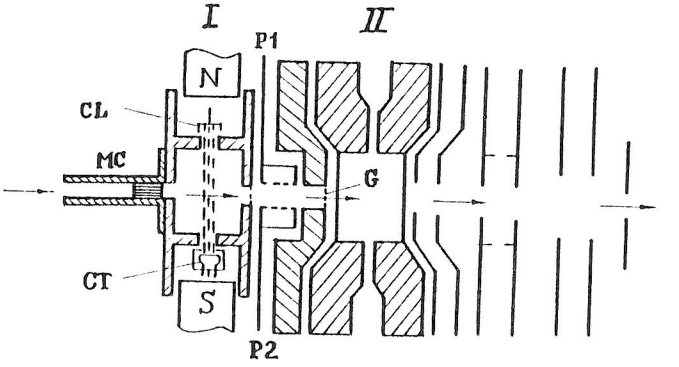

Fig. 1. Schematic of the two-chamber ion source: I,II, excitation and collision chambers; MC, multichannel inlet capillary; CT, cathode; CL, collector; P1,P2, deflection plates; G, metallic grid.

3. RESULTS

The present investigation has discovered that binary mixture inlet leads to formation of complex ions $Ar^{14}NO^+$, $Ar^{15}NO^+$, $Kr^{14}NO^+$, $Kr^{15}NO^+$, $Xe^{14}NO^+$, $Xe^{15}NO^+$, $ArCH_3OH^+$ and $ArC_6H_6^+$ in addition to ions produced as a result of penning and dissociative ionization and ionization of highly excited atoms on metal surface. To establish the processes involved the complex ion current dependences were obtained on mixture total pressure (quadratic), component partial pressure (linear), electron emission current (linear) and exciting electron energy. Linearity of ion currents on partial pressures and electron current indicated the single collision condition. Data analysis leads to an unambiguous conclusion that the complex ions observed are formed in reactions of association ionization $R^m + M \rightarrow RM^+ + e$ resulting from collisions of metastable atoms $Ar^m(^3P_2, ^3P_0)$, $Kr^m(^3P_2, ^3P_0)$ and $Xe^m(^3P_2, ^3P_0)$ with unexcited gas target molecules since the appearance thresholds for these ions coincide with the appearance thresholds for respective metastable atoms (5)(Fig. 2). Ionization functions for the complex ions correlate well with the metastable state excitation functions of respective noble gas atoms. The highly excited noble gas atoms do not contribute to complex ion formation that is seen from a great difference between excitation functions of atomic Rydberg states (6) and corresponding ionization functions for the complex ions under study. Relative intensities of complex ions (with respect to the intensities of molecular ions generated by penning ionization) are as follows: 37.6% for $ArNO^+$, 35.4% for $KrNO^+$, 4% for $XeNO^+$, 2% for $ArCH_3OH^+$ and 1% for $ArC_6H_6^+$ that proves a significant probability of association ionization in collisions of metastable krypton, argon and xenon atoms with the NO, CH_3OH and C_6H_6 molecules. For ^{14}NO and ^{15}NO,

no isotope effect was observed. No association ionization was detected in binary mixtures of helium and neon atoms with the molecules.

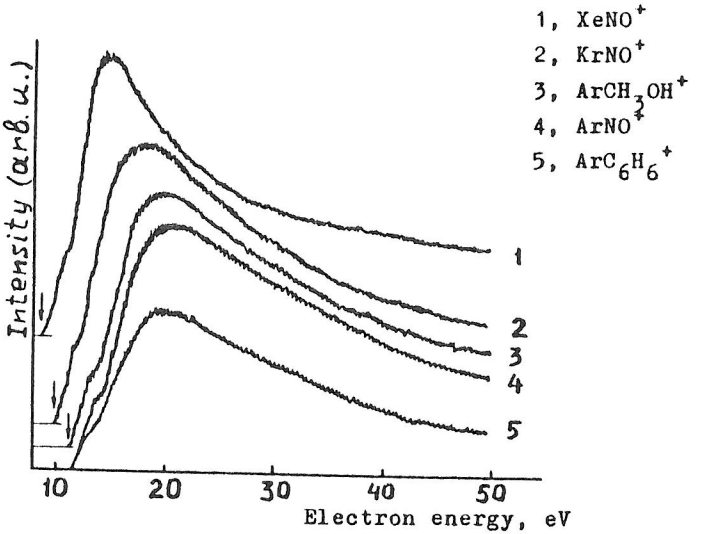

Fig. 2. Ionization functions for complex ions.

The penning and association ionization studied can be represented in terms of autoionization of "superexcited" quasimolecules of the type RM^{xx}. Depending on the energy taken away by the emitted electron, the RM^+ ions can be formed stable or be dissociated to M^+ ions and noble gas atoms.

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