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Abstract

Full Text

PHYSICAL CHEMISTRY

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ON THE SPONTANEOUS AND INDUCED DECAY OF DOUBLY CHARGED IONS

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In studying the dissociation of doubly charged ions $C_2H_4^{2+}$, $C_2H_3^{2+}$, and $C_2H_2^{2+}$, we found that some of these ions decay spontaneously, i.e., without interaction with target molecules.

The investigations were carried out on a double mass spectrometer, the scheme and description of which are given in work (^{1}). The ions $C_2H_4^{2+}$, $C_2H_3^{2+}$, and $C_2H_2^{2+}$ were obtained by ionization of ethylene with electrons of energy 130 eV. To elucidate the mechanism of the process of secondary-ion formation, we studied the influence of the energy of the ionizing electrons in the ion source and of the gas pressure in the collision chamber on the intensities of the primary ions $C_2H_4^{2+}$, $C_2H_3^{2+}$, $C_2H_2^{2+}$, and of the secondary ions $C_2H_4^+$, $C_2H_3^+$, $C_2H_2^+$, C_2H^+, C_2^+. It was established that, when the electron energy is increased, ions $C_2H_3^{2+}$ begin to appear at about 36 eV. The appearance of these ions can be accurately identified, since their mass-to-charge ratio (m/q) is equal to 13.5. Therefore no other ions from ethylene are superimposed on them. Together with the ions $C_2H_3^{2+}$, secondary ions $C_2H_3^+$, $C_2H_2^+$, C_2H^+, and C_2^+ also appear, formed as a result of inelastic processes occurring with the ions $C_2H_3^{2+}$ in the space between the two magnetic analyzers. The appearance potential of the ions $C_2H_3^{2+}$ in collisions of electrons with ethylene molecules, as shown in (^{2}), is 36.2 eV, which agrees with our measurements.

Fig. 1. Influence of pressure on the ratio of the intensity of secondary ions $C_2H_3^+$, formed upon dissociation of ions $C_2H_4^{2+}$, to the intensity of primary ions $C_2H_4^{2+}$.

At an electron energy of 32 ± 1 eV, secondary ions $C_2H_4^+$, $C_2H_3^+$, $C_2H_2^+$, C_2H^+,

Fig. 2. Proposed potential curve of the doubly charged ion $C_2H_4^{2+}$

Figure 2: Fig. 2. Proposed potential curve of the doubly charged ion $C_2H_4^{2+}$

and C_2^+ begin to appear, caused by inelastic processes occurring with the ions $C_2H_4^{2+}$. The appearance potential of the ions $C_2H_4^{2+}$ is unknown in the literature, since in the mass spectrometer these ions are overlapped by ions CH_2^+.

The dependences of the ratio of the current I^* of secondary ions to the current I of the initial ions on the change in air pressure in the collision chamber show (Fig. 1) that the ions $C_2H_4^{2+}$ decay not only as a result of single collisions with molecules, but also spontaneously. The ions $C_2H_3^{2+}$ and $C_2H_2^{2+}$ behave analogously.

The spontaneous decay
$C_2H_4^{2+} \rightarrow C_2H_3^+ + H^+$
of ions $C_2H_4^{2+}$ can be interpreted as a process in which a proton passes through a potential barrier (tunnel effect). Indeed, one may suppose, as was done

(3) for other doubly charged ions, that the potential-energy surface of the lower electronic state of the ion $C_2H_4^{2+}$ will have a not quite ordinary form because of the superposition, on the chemical bond $C_2H_3^+ - H^+$, of the mutual Coulomb repulsion of the ions $C_2H_3^+$ and H^+. A schematic section of this potential surface in a plane passing through one of the coordinates is shown in Fig. 2. In view of the large difference between the electron shells of C_2H_4 molecules and the $C_2H_4^{2+}$ ions formed from them by electron impact, one should expect the presence in the $C_2H_4^{2+}$ ions of vibrational excitation E. This facilitates penetration of the proton through the potential barrier, since it reduces its effective height $(V - E)$ and width "a." Of course, other decay mechanisms may also make some contribution to the spontaneous dissociation of doubly charged ions. However, the mechanism considered is, in our opinion, the principal one. An analogous consideration applies also to the processes $C_2H_3^{2+} \rightarrow C_2H_2^+ + H^+$, $C_2H_2^{2+} \rightarrow C_2H^+ + H^+$ of decay of the ions $C_2H_3^{2+}$ and $C_2H_2^{2+}$, respectively.

Fig. 2. Proposed potential curve of the doubly charged ion $C_2H_4^{2+}$

The potential-energy curve analogous to that shown in Fig. 2 was obtained (3) for the lower electronic state of the ion CO^{2+}. It may be expected that CO^{2+} ions in this state should decay spontaneously. Earlier, upon the observation (4) of dissociation of CO^{2+} ions in a mass spectrograph, this was in fact assumed, although no experimental evidence was given. However, a later investigation (5) did not confirm this. It was shown that CO^{2+} ions dissociate only as a result of collisions with atoms and molecules. There may be several reasons for the discrepancy between the results of works (4) and (5); at least two can be cited: 1) the probability of producing CO^{2+} ions under the conditions of work (5) in the required state is small; 2) the half-life of CO^{2+} ions is large, $\gtrsim 10^{-5}$ sec, so that, during the limited time under the experimental conditions of that work, the contribution of spontaneous decay to the total probability of dissociation is insignificant. This reason is quite substantial, taking into account the large mass of C^+, which hinders permeability of the barrier. In any case, the question of the decay of the CO^{2+} ion deserves additional study.

Dissociation of the ions $C_2H_4^{2+}$, $C_2H_3^{2+}$, and $C_2H_2^{2+}$ also occurs as a result of single collisions with molecules. Therefore, the effective cross sections of these processes can be determined. However, this possibility exists only for the case of dissociation of $C_2H_3^{2+}$ ions, since the other ions ($C_2H_4^{2+}$ and $C_2H_2^{2+}$) are registered with superposition of the ions CH_2^+ and CH^+, respectively.

The effective cross sections of dissociation upon collision with air molecules of $C_2H_3^{2+}$ ions having an energy of 9000 eV were found to be as follows:

$$C_2H_3^{2+} \to C_2H_2^+ \; - \; 0.8 \cdot 10^{-15} \text{ cm}^2$$

$$C_2H_3^{2+} \to C_2H^+ \; - \; 3.5 \cdot 10^{-16} \text{ cm}^2$$

$$C_2H_3^{2+} \to C_2^+ \; - \; 1.1 \cdot 10^{-16} \text{ cm}^2$$

The cross section of the process of electron capture by the $C_2H_3^{2+}$ ion upon collision with an air molecule is equal to $\sim 1.7 \cdot 10^{-15}$ cm^2. The cross sections σ were determined by the for-

formula:

$$\sigma = \frac{I^* kT}{I \cdot P \cdot l}, \qquad (1)$$

where P is the absolute pressure in the collision chamber, and l is its effective length.

The random error, determined from the reproducibility of the cross-section values, does not exceed $\sim 20\%$. However, the values of the measured effective cross sections may be systematically underestimated by approximately 30% because of the lower efficiency of collecting secondary ions as compared with the primary ions $C_2H_3^{2+}$. This is caused mainly by a certain change, occurring in the inelastic process (dissociation, electron capture), in the velocity of the secondary ions; this applies especially to ions formed by the removal of a larger number of hydrogen atoms.

As can be seen, the cross-section values, in particular for the process of electron capture by $C_2H_3^{2+}$ ions and dissociation with the formation of $C_2H_2^+$, are quite large.

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Physicochemical Institute
named after L. Ya. Karpov

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Note: Figure translations are in progress. See original paper for figures.