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Abstract

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Mass-Spectrometric Detection of Reactions of Highly Excited Hydrogen Atoms with Ethylene Molecules

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When electrons collide with ethylene molecules, various ions, molecules, atoms, and radicals are formed. The former are detected directly in the mass spectrum of ethylene. Thus, for example, when electrons with an energy of 70 eV collide with ethylene molecules, the following ions are formed (^1): $C_2H_4^+$ –100% (10.5 eV), $C_2H_3^+$ –67.9% (14.0 eV), $C_2H_2^+$ –67.5% (13.5 eV), C_2H^+ –13.5% (19.3 eV), C_2^+ –4.62% (26.5 eV), CH_2^+ –7.83% (19.3 eV), CH^+ –4.68% (23.0 eV), C^+ –3.17% (24.7 eV), H_2^+ –0.88% (22.5 eV), H^+ –6.71% (26.3 eV). In parentheses are given the appearance potentials of these ions (^2). There are no direct data on the processes of formation of neutral particles in this case. However, some conclusions can be drawn. For example, when $C_2H_3^+$ ions are formed, hydrogen atoms are formed approximately* in the same amount. When $C_2H_2^+$ ions are formed, both atoms and molecules of hydrogen are formed with approximately equal probability (^4). In the processes of formation of other ions, hydrogen atoms and molecules, as well as various radicals, are formed (^5).

It may be assumed that neutral particles are formed not only in processes with simultaneous formation of ions, but also in processes of dissociation of ethylene molecules. Similar reactions in the collision of electrons with propane and butane molecules have been studied (^6). In such processes, neutral particles may be formed both in the ground state and in various states of electronic and vibrational excitation.

There are no data on reactions of ethylene molecules with electronically excited neutral products of dissociation of these molecules. This can be explained by the fact that, in the mass-spectrometric method, ions are recorded, while for the formation of ions in reactions of neutral particles it is necessary that at least one of the reacting particles be highly excited.

The formation of long-lived highly excited particles upon collision of electrons with ethylene molecules had not been observed until recently. Only recently have we detected (^7) H and C atoms in such states. Ethylene molecules in long-lived highly excited states were not detected in appreciable amounts (^7, ^8). This may indicate that most highly excited states of the ethylene molecule

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

are unstable, or that electronic transitions occur into the region above the dissociation limit of stable states.

Below are presented the results of a study of reactions in ethylene involving highly excited H atoms. Considerably fewer highly excited C atoms are formed than H atoms; therefore their role in the processes considered below is apparently small. Owing to the fact that the excit–

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* A small fraction of $C_2H_3^+$ ions is formed (^3) as a result of the decay of doubly charged ions
$C_2H_4^{2+} \rightarrow C_2H_3^+ + H^+$.

hydrogen atoms H are in states with a large* principal quantum number; they are long-lived ([9]). This makes it possible to study reactions involving such atoms at a comparatively low pressure ($\sim 10^{-4}$ torr).

The investigation was carried out on a mass spectrometer with a two-chamber ion source. The layout of the ion source and the operating procedure are given in ([7]). In the first chamber of the ion source, excitation and ionization of ethylene molecules were produced by an electron beam of adjustable energy. The ions formed were retained in the first chamber by electric and magnetic fields.

Fig. 1. Effect of ethylene pressure on the relative ion intensity. I/P is the ratio (in arbitrary units) of the ion current I to the pressure P. 1 –$C_2H_4^+$, 2 –$C_2H_3^+$, 3 –$C_2H_2^+$, 4 –H^+, 5 –C^+. Dependences 4 and 5 are given on an arbitrary scale. Electron energy $E_e = 60$ eV.

Fig. 2. Effect of the electron energy E_e on the intensity I (in arbitrary units) of ions: 1 –$C_2H_4^+$, 2 –$C_2H_3^+$, 3 –$C_2H_2^+$, 4 –H^+, 5 –C^+. The curves were recorded automatically with an EPP-09 electronic potentiometer. The ethylene pressure, read from the indications of an LM-2 lamp, was $1.2 \cdot 10^{-4}$ torr. Dependences 4 and 5 are given on an arbitrary scale.

Only neutral particles entered the second chamber, located at a distance of ~ 5 mm from the first chamber. Under these conditions, at a pressure of $\sim 5 \cdot 10^{-5}$ torr, mainly H^+ and C^+ ions were extracted from the second chamber. When the ethylene pressure in the ion source was increased, other ions also appeared, among which the most intense were $C_2H_4^+$, $C_2H_3^+$, and $C_2H_2^+$.

To determine the mechanism of formation of these ions, we studied the effect

on their intensity of the ethylene pressure and of the energy of the electrons exciting the gas in the first chamber of the ion source. The purpose of the first study was to determine the type of reaction; the purpose of the second was to identify the reacting particles. The results are shown in Figs. 1 and 2. They are reproduced with an accuracy of $\pm 15\%$.

From the dependences, shown in Fig. 1, of the relative intensities of various ions on the ethylene pressure, it may be concluded that the ions $C_2H_4^+$,

* In these experiments the hydrogen atoms must be in states whose principal quantum number is $n \geqslant 6$, since all lower states have insufficiently long lifetimes ($\sim 10^{-8}$-10^{-9} s) ([9]).

$C_2H_3^+$ and $C_2H_2^+$ are formed as a result of bimolecular reactions. Their intensity I is directly proportional to the square of the pressure P of ethylene, i.e.,

$$I = kP^2, \tag{1}$$

where k is a constant.

The intensity of H^+ ions varies with the pressure of ethylene in accordance with the expression

$$I = nP + mP^2, \tag{2}$$

where n and m are constants. The first term in this formula characterizes the formation of H^+ ions as a result of ionization of highly excited hydrogen atoms on the metal surface Me in the process:

$$H^* + Me \rightarrow H^+ + Me. \tag{3}$$

The second term of formula (2) describes the process of formation of H^+ ions as a result of collisions of highly excited hydrogen atoms with ethylene molecules according to the scheme

$$H^* + C_2H_4 \rightarrow H^+ + C_2H_4 + e. \tag{4}$$

This process is energetically possible only with those hydrogen atoms which are not only highly excited but also have appreciable kinetic energy, since reaction (4) is endothermic. Taking into account that the endothermicity of this reaction is not large (< 0.4 eV) and that hydrogen atoms may have kinetic energies of ~ 1 eV and more, one may understand the significant role of reaction (4) in the process of formation of H^+ ions (Fig. 1). C^+ ions, as can be seen from the dependences in Fig. 1, are formed mainly by a reaction of type (3).

From the dependences shown in Fig. 2 it can be seen that $C_2H_4^+$, $C_2H_3^+$, and $C_2H_2^+$ ions appear at an electron energy close to 18 eV. At this energy H^+ ions

also appear. From the dependences shown in Figs. 1 and 2 one may conclude that $C_2H_4^+$, $C_2H_3^+$, and $C_2H_2^+$ ions are formed as a result of the following processes. Upon collision of electrons with ethylene molecules in the first chamber of the ion source, highly excited hydrogen atoms are formed by the reaction

$$C_2H_4 + e \rightarrow H^* + [C_2H_3] + e. \quad (5)$$

In the second chamber of the ion source, these hydrogen atoms ionize ethylene molecules in the process

$$C_2H_4 + H^* \rightarrow C_2H_4^+ + H + e. \quad (6)$$

The energy released in the collision of highly excited hydrogen atoms with ethylene molecules is sufficient for the formation of $C_2H_2^+$ ions in the process

$$C_2H_4 + H^* \rightarrow C_2H_2^+ + H_2 + H + e. \quad (7)$$

However, this energy is insufficient for the formation of $C_2H_3^+$ ions. These ions appear as a result of a more complex reaction

$$C_2H_4 + H^* \rightarrow C_2H_3^+ + H_2 + e, \quad (8)$$

in which the hydrogen atom is captured and a hydrogen molecule is formed.

In generalized form, reactions (6), (7), (8) may be represented as follows. Upon collision of an excited hydrogen atom with an ethylene molecule, a superexcited, short-lived ethyl radical $C_2H_5^*$ is formed. The decomposition of this radical may proceed by two routes: 1) autoionization and decomposition of the excited $C_2H_5^+$ ion into $C_2H_4^+$, $C_2H_3^+$, $C_2H_2^+$ ions and neutral H_2 molecules and H atoms; 2) dissociation of the ethyl radical into atoms and molecules of hydrogen and neutral superexcited fragments $C_2H_4^*$, $C_2H_3^*$, $C_2H_2^*$, which subsequently autoionize.

At present it is difficult to give preference to any one of these schemes, since the ratio between the rates of autoionization and dissociation is not known, and it is precisely this that is decisive in the present case. If these rates are of the same order, then both decomposition schemes occur. The second

scheme may lead to decomposition into smaller fragments without the formation of ions.

From the dependences shown in Fig. 2 it can be seen that highly excited hydrogen atoms are formed by several pathways. On curve 4 a break is clearly seen at an electron energy of about 30 eV. A smaller break occurs near 39 eV. The appearance of H* atoms at $E_e \sim 18$ eV is due to process (5), in which stable radicals C_2H_3 are formed. At higher electron energies, H* atoms may be formed simultaneously with the dissociation of C_2H_3 radicals and even with

their ionization or the ionization of their fragments. For example, the break in curve 4 of Fig. 2 near 30 eV can, energetically, be associated with the following dissociation processes of the ethylene molecule: $C_2H_4 \rightarrow H^* + 3H + C_2$, $H^* + 2H + C + CH$, $C_2H_3^+ + H^*$, $H + H^* + C_2H_2^+$, and other processes.

The break in curve 4 of Fig. 2 near 30 eV appears on curves 1, 2, and 3, corresponding to the formation of the ions $C_2H_4^+$, $C_2H_3^+$, and $C_2H_2^+$. It can be seen that highly excited hydrogen atoms formed by electrons with energies in the range 18-30 eV are quite reactive for the formation of the ions $C_2H_4^+$, $C_2H_3^+$, and $C_2H_2^+$, and are only slightly effective for the formation of H^+ ions. At higher electron energies there is a large increase in the yield of H^+ ions and only a slight increase in the yield of the ions $C_2H_4^+$, $C_2H_3^+$, and $C_2H_2^+$. The explanation for this should be sought in the influence of the kinetic energy of H* atoms on the processes of formation of the ions H^+, $C_2H_4^+$, $C_2H_3^+$, and $C_2H_2^+$. At electron energies $E_e > 30$ eV, the new processes of formation of H* atoms are such that these atoms have a kinetic energy somewhat greater than in the processes of their formation at $E_e < 30$ eV. As a result, the H* atoms reach the second chamber more rapidly and, in addition, the effectiveness of process (4) increases, which leads to a sharp break in curve 4 of Fig. 2. The change in curves 1, 2, and 3 occurs to a lesser extent, since an increase in the kinetic energy of H* atoms not only does not promote the formation of ethyl radicals, but even hinders it.

The present work may prove useful for understanding various processes in radiation chemistry and plasma chemistry, since it provides experimental evidence for the occurrence of the process of formation of hydrogen atoms and molecules simultaneously with ions in reactions of slow neutral particles. Evidently, when highly excited hydrogen atoms collide with molecules, processes requiring less energy also occur, i.e., processes of molecular dissociation without the formation of ions, but with the formation of active atoms, molecules, and radicals capable of initiating synthesis reactions. Less excited atoms may also take part in such processes, since in terms of energy they differ comparatively little from highly excited atoms (by $\sim$ 2–4 eV). A large difference, as noted above, exists in the lifetimes of these states. However, under real radiation-chemical conditions (in gases at high pressure, and even more so in liquids and solids) the time parameter is far less significant, since under these conditions the radiative lifetimes of even low excited states are $\sim$ 3–4 orders of magnitude longer than the time between collisions of molecules. In general, the role of excited particles in such processes appears to be substantial.

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