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IONIZATION AND DISSOCIATIVE IONIZATION OF GLYCERIN MOLECULES BY ELECTRON IMPACT NEAR THRESHOLD

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Abstract. Method of measurement of functions of dissociative ionization of glycerin molecules is described, their relative cross-sections being obtained. The experiment was carried out by the method of crossing electron and molecular beams using a setup with a monopole mass spectrometer. A secondary electron multiplier was used for ion detection. The glycerin molecule mass spectrum is presented as well as the energy dependences of disociative ionization cross-sections in the range $5 - 40\ eV$, from which the fragment ion appearance thresholds are determined.

1. INTRODUCTION

Here we present the results of experimental studies of dissociative ionization of glycerin (1,2,3-trihyroxypropane, $C_3H_8O_3$) molecule by electron impact in the near-threshold energy range. Along with methanol, ethanol, methyl and ethyl esters of fatty acids as well as terpenoids, glycerin is treated as a potential fuel to replace the oil product fuel. Glycerin is the simplest representative of triatomic alcohols. Due to the presence of three OH groups in the molecule, it gives threerows of derivatives. Note that the mono- and di-derivatives can exist in the form of two structural isomers and the derivatives of $CH_2XCHOHCH_2OH$ or $CH_2XCHXCH_2OH$-type – in the form of optical isomers. Ionization of molecules by electron impact plays an important role in the processes in low-temperature plasma, especially in non-equilibrium gas discharge plasma. The products of dissociative ionization of multiatomic molecules can be various atomic and molecular ions being contained in the initial molecule:

$$e + \mathrm{XYZ} \Longrightarrow (\mathrm{XY})^+ + \mathrm{Z} + 2e \quad \text{or} \quad e + \mathrm{XYZ} \Longrightarrow \mathrm{X} + (\mathrm{YZ})^+ + 2e. \quad (1)$$

As a rule, at a collision of an electron with a molecule, an unstable molecular ion is formed which subsequently decays into more simple fragments, fragment ions, neutral residue. Therefore, dissociative ionization of multiatomic molecules can proceed in different channels, producing different dissociation products: fragment ions and neutral atoms or molecules.

A number of papers has been devoted to theoretical and experimental studies of ionization of complex organic compounds by electron impact; however, they are mainly concentrated on the determination of ionization potentials (IPs) of the parent molecule and appearance potentials (APs) of fragment ions being formed due to the dissociative ionization. Allam et al. (1982) have analyzed the initial sections of the ionization curves of some molecules in order to use them to determine the APs of fragment ions. As regarding investigation and analysis of the threshold behaviour of the fragment ions being formed as a result of the dissociative ionization, there are much less data available and there a practically no data for alcohol molecules. The most efficient method of studies of ionization, including dissociative ionization, is mass spectrometry, enabling both the information on the mass spectrum of the molecule under investigation to be obtained and the relative contribution of each of the dissociated fragments into the formation of ions to be evaluated at the same experimental conditions.

2. EXPERIMENT

The experiment was carried out using a setup with a monopole mass spectrometer, the method of crossing electron and molecular beams being employed (Zavilopulo et al. 2002). The molecular beam was formed by evaporating the investigated substance from a liquid state using an effusive multichannel source of neutral particles. The concentration o molecules in the area of interaction with the electron beam was not lower than $10^{11} - 10^{12}\ cm^{-3}$ at the residual gas pressure in the setup of $\sim 10^{-6}\ Torr$. In order to avoid condensation of the substance under investigation on the vacuum chamber walls and the mass spectrometer electrodes, the mass analyzer chamber was heated to the temperature $\sim 150 - 200^oC$. Molecules become ionized in an ion source with electron bombardment. This source enables the electron beams of controlled energy to be obtained in the electron current stabilization mode at the current values $0.5 - 1.5\ mA$ at the energy spread not worse than $\triangle E = 500\ meV$ (full width at half maximum). The ions, extracted from the source, are focused into a beam, move to the analyzer (mass filter) electrode area, separated according to their mass and detected by a secondary electron multiplier or an ion collector in the form of a Faraday cup. The mass scale was calibrated using the mass lines of N_2, Ar, and Kr.

3. DISCUSSION

Aliphatic polyols are easily decomposed, the decomposition being accompanied by dehydratation and dehydration. A specific feature of their mass spectra is a low intensity of the molecular ion peak or its total absence. The most common trend of fragmentation is simple breakdown of hydrocarbon skeleton bonds with the formation of oxonium type ions as well as dehydratation of the molecular and fragment ions. Formation of oxonium ions at the fragmentation of aliphatic alcohols can be a result of charge localization on the oxygen atom and β-decay of the molecular ion (with respect to the heteroatom). Processes of formation of water and oxonium cations are competitive, in this case not only the molecular ion, but also the hydroxyl-containing ions being subject to dehydratation (Zenkevich et al. 1986).

In the glycerin molecule mass spectrum, experimentally obtained at the ionizing electron energy $70\ eV$ (Fig.1), there is no molecular ion at all. The high specific fragmentation depth of the initial molecule is confirmed by the formation of fragments with small masses, and low selectivity of the spectrum shows the absence of predomi-

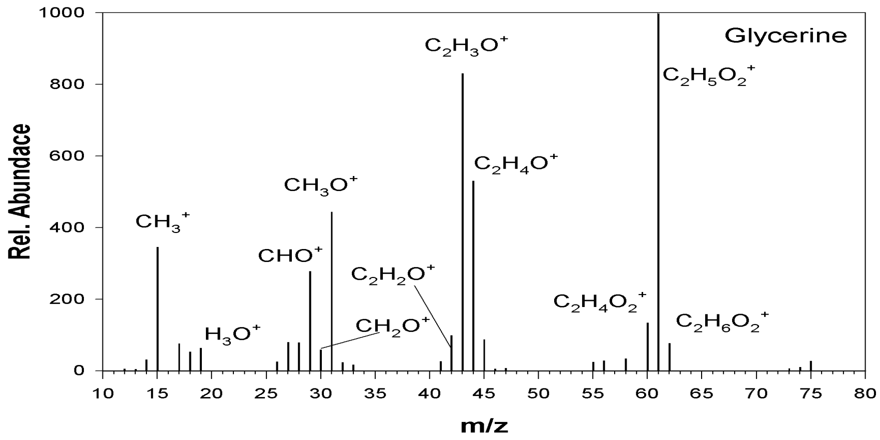

Figure 1: Glycerin molecule mass spectrum ($E = 70\ eV$).

nant trends of decomposition of the molecular ion. The most intense peaks correspond to the peaks of the oxonium ion $[HOCH_2CH{=}OH]^+$ with $m/z = 61$, $[H_2C{=}C{=}OH]^+$ ($m/z = 43$), $[H_2CCH{=}OH]^+$ ($m/z = 44$), and $[H_2C{=}OH]^+$ ($m/z = 31$) as well as to the products of secondary fragmentation of $[CO]^+$ and $[CH_3]^+$ fragment ions. High hygroscopicity of glycerin and the presence of three OH groups in a molecule result in the formation of considerable amounts of molecular water and hydroxonium ions ($m/z = 18$ and 19). The maximal intensity in the mass spectrum corresponds to the $[C_2H_5O_2]^+$ ion with $m/z = 61$ which is complementary to the $[CH_3O]^+$ ion ($m/z = 31$). This pair of ions is formed at a simple breakdown of the C–C bond of the glycerin molecule, the charge being localized mostly at a fragment with larger molecular mass. The low probability of fragmentation processes, in which the single-charged molecular ion is decomposed into a light uncharged ion and a heavy charged ion according to Afrosimov et al. (2006), is explained by the fact these processes having higher ionization threshold energy than the processes with the formation of a light charged fragment and a light neutral fragment.

Having tuned the spectrometer for transmission of ions of a certain mass, we have measured the energy dependences of cross-section of dissociative ionization of fragments in the energy range $5 - 40\ eV$, a special attention being given to the initial parts of the ionization curve. Energy scale calibration was performed by measuring well known threshold parts of ionization functions for nitrogen molecule and krypton atoms (Zavilopulo at al. 2002). The calibration procedure was repeated at each measurement cycle, thus providing energy scale determination accuracy comparable with the half-width of the energy spread for the electrons within the beam.

As known from Cherny at al. (1995), determination of the ionization energy for organic molecules is a complicated problem. Among the two known methods, photoionization (PI) and electron-impact ionization (EI), the second one is more universal and can be applied for a wide class of atoms and molecules. Besides, the PI methods has essential restrictions regarding the studies of dissociative ionization process. The EI method is based on the determination of a point in the energy dependence of the

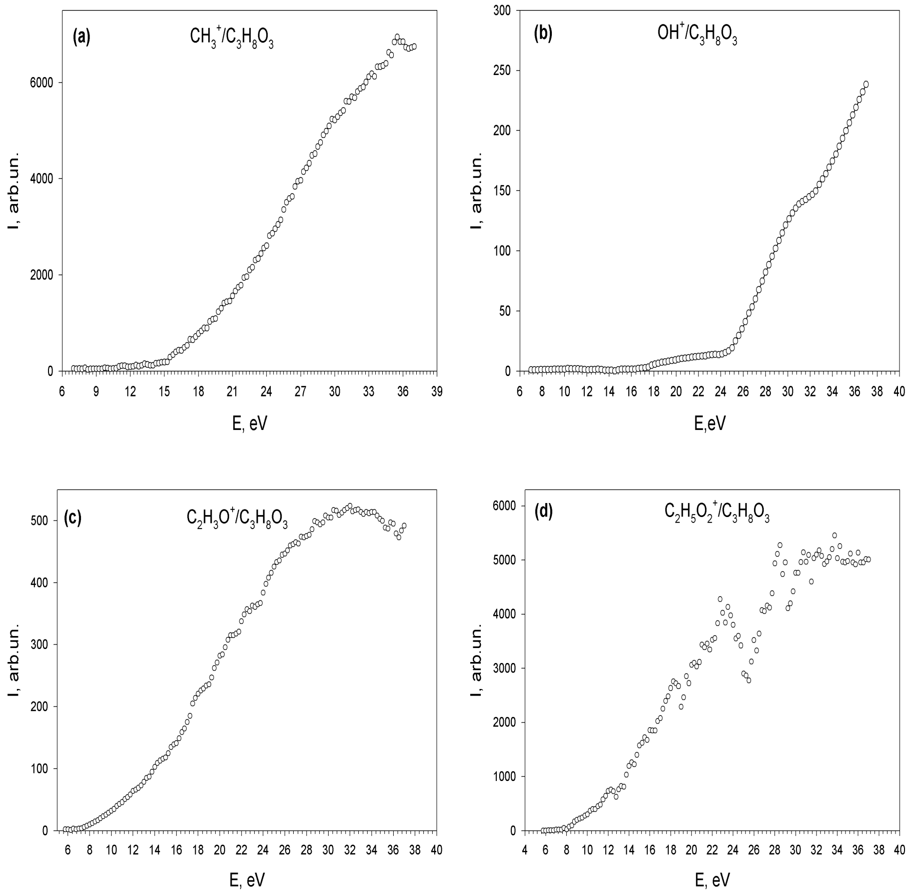

Figure 2: Energy dependenes of relative cross-sections of dissociative ionization of some child ions of the glycerin molecue.

ionization cross-section, starting from which the cross-section becomes non-zero. The accuracy of determination of this energy is affected by three main factors:

- ionization cross-section rate versus bombarding electron energy;
- electron monoenergetic beam;
- accuracy of electron energy scale calibration.

Thus, a certain procedure should be applied to the measured energy dependence of the cross-section of dissociative ionization of a fragment, minimizing the effect of these factors. One of the most well known is the procedure of double differentiation of the initial parts of ionization functions using the Lossing method with digital filtration and fitting of the obtained curve according to the Breit-Wigner formula. The most exact and widely applied is a least-square method of fitting of the initial part of the ionization curve using the Marquardt-Levenberg algorithm proposed by Fiegele et al. (2000).

Table 1: Appearance potentials of ion fragments at the dissociative ionization of glycerin molecules

fragment ions	m/z	E_{ap} (eV)
CH_3^+	15	15.31 ∓ 0.25
OH^+	17	18.12 ∓ 0.25
H_3O^+	19	12.12 ∓ 0.25
CO^+	28	10.89 ∓ 0.25
CHO^+	29	12.20 ∓ 0.25
CH_3O^+	31	12.37 ∓ 0.25
$C_2H_2O^+$	42	7.80 ∓ 0.25
$C_2H_3O^+$	43	7.23 ∓ 0.25
$C_2H_4O^+$	44	7.60 ∓ 0.25
$C_2H_4O_2^+$	60	8.10 ∓ 0.25
$C_2H_5O_2^+$	61	7.43 ∓ 0.25
$C_2H_6O_2^+$	62	7.27 ∓ 0.25

Energy dependences of relative cross-sections of dissociative ionization of some child ions of the glycerin molecule in the energy range $5 - 40$ eV are shown in Fig. 2. These dependences were used to determine the appearance potentials (E_{ap}) for practically all fragment ions using the method proposed by Fiegele et al. (2000) (See Table 1). One should pay attention to the low values of appearance thresholds for dissociative ionization fragments $[C_2H_3O]^+$ and $[C_2H_5O_2]^+$. Evidently, the formation of the fragment ion with $m/z = 43$ occurs at the elimination of a water molecule from the $[C_2H_5O_2]^+$ ($m/z = 61$) ion. Such low values of the appearance potentials for these fragments are explained by a change of geometry and interatomic distances in an ionized molecule in comparison with a neutral one, resulting in an essential decrease of the C–C binding energy in the ionized molecules (Afrosimov et al. 2006, Johnstone 1972). Note that the behaviour of relative ionization cross-sections in the energy range $5 - 40$ eV for these fragment ions is different (Fig. 2c, d): while for the $[C_2H_3O]^+$ fragment ion a gradual growth is observed with a smooth maximum at $E_i = 32$ eV, for $[C_2H_5O_2]^+$ several distinct maxima at $E_i = 12, 18, 24, 28$, and 32 eV are revealed.

The energy dependence of the relative cross-section of dissociative ionization of the $[OH]^+$ ion (Fig.2,b) is stepwise, the threshold value E_{ap} for this ion corresponding to the appearance threshold for the $[OH]^+$ ion at dissociative ionization of water molecule. A sharp increase of yield of this ion at 24 and 32 eV, probably, corresponds to stage-like splitting this ion off the products of primary dissociative ionization of the glycerin molecule. The appearance potential of the $[CH_3]^+$ ion also testifies for the formation of this fragment as a result of secondary dissociation, accompanied by migration of a proton. For the energy dependence of this fragment ion yield an almost linear growth is observed from the appearance potential to 36 eV (Fig. 2, a).

Thus, we present the first data regarding the appearance thresholds for fragments of dissociative ionization of the glycerin molecule. Splitting the electron off the neutral $C_2H_5O_3$ molecule at the ionization results in an essential relaxation of interatomic bonds in the hydrocarbon skeleton which affects the threshold parts of the energy dependences and the absolute values of appearance potentials of the fragment ions measured.

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