ELECTRON IMPACT IONIZATION OF ETHYLENE GLYCOL MOLECULE

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Mass spectrometric studies of the positive ion yield due to the electron impact ionization of ethylene glycol molecules in the gas phase have been carried out. The ionization energy of a molecule and the energies of appearance of basic fragment ions have been obtained based on the ionization efficiency curves. The value of the ionization energy for a $C_2H_6O_2$ molecule has been determined experimentally to be (10.21 ± 0.25) eV. The experimental values of the energies of appearance for the basic fragment ions with $m/z = 31$, 33, and 29 have been found to be (11.13 ± 0.25), (10.56 ± 0.25), and (17.79 ± 0.25) eV, respectively.

1. Introduction

A high interest in the study of the processes of interaction of slow electrons with alcohol molecules is induced, first of all, by their wide industrial application. In addition, the discovery of such molecules in the interstellar space and in planet atmospheres [1–3] provokes interest from the viewpoint of fundamental science in the questions of the origin and the radiation stability of organic substances, as well as the importance of these processes for understanding the nature of the radiation-induced damage of biological objects [4]. The majority of researches [5,6] of the interaction of electrons with alcohol molecules concerns methanol (CH_3OH), ethanol (C_2H_5OH), propanol (C_3H_7OH), butanol (C_4H_9OH), and allyl alcohol (C_3H_5OH). The electron impact dissociative ionization of alcohols was studied in [7,8] in detail. For all the investigated alcohols, one observed the following groups of fragment ions: H_y, CH_y, C_xH_y, CH_yO, and C_xH_yO, where x and y can takes various values.

This work reports the results of mass spectrometric studies of the processes of dissociative ionization of ethylene glycol molecule by slow electrons. In spite of the rather large industrial importance of this representative of diatomic alcohols, the literature on the interaction of electrons with various energies with alcohol molecules practically does not include the studies of ethylene glycol molecules by means of electron-impact mass spectrometry representing the most widespread ionization method in modern mass spectrometers. The main advantages of this method are its reliability and universality. In addition, the existing computer libraries of mass spectra (Wiley and NIST) adduce the spectra obtained under the action of electron impact as recommended ones.

2. Experiment

The experiment was performed on a set-up with the oil-free згьзштп of residual gases. As an analytical device, we used a monopole mass spectrometer MX-7304A [9] with the digital indication of the mass number and the intensity of ion peaks. It can operate in the modes of manual, cyclic, and programmable sweeps of the mass spectrum and energies of ionizing electrons. A more detailed description of the experiment can be found in [10]. Here, we discuss only its basic points. A beam of studied molecules was formed with the help of a multichannel source of the effusion type providing a molecular concentration of 10^{10}–10^{11} cm^{-3} in the region of interaction with an electron beam. The ion source with electron ionization operated in the mode of stabilization of the electron current and allowed one to obtain electron beams with a fixed energy at currents of 0.5–1.5 mA and the energy spread $\Delta E = 500$ meV. The mass scale was calibrated using Ar and Xe beams, while the scale of electron beam energies was graduated with respect to the initial region of the ionization cross section of

Kr atoms. The experimentally measured dependences of the ionization cross section on the energy of ionizing electrons were used to determine the energies of appearance of basic fragments of ethylene glycol molecule. The experiment consisted of two parts: in the first one, we measured the mass spectra in the mass range 0–80 amu at the ionization energies $E_i = 20$–100 eV; while, in the second one, we studied the energy dependences of the relative cross sections of dissociative ionization in the range of ionizing electron energies 5–40 eV.

3. Discussion of the Results

The electron impact ionization of ethylene glycol molecules ($C_2H_6O_2$) results in the formation of a certain number of positive ions that increases with the ionizing electron energy. Figure 1 presents the mass spectra of positive ions obtained at various electron energies. In this figure, one observes a change of the fragmentation depth of the initial molecule that depends considerably on the energy of bombarding electrons. In particular, at an ionizing electron energy of 30 eV (Fig. 1,a), the highest intensity in the spectrum is revealed by two peaks corresponding to ion-fragments with $m/z = 31$ and 33, whereas the intensity of other fragment ions is less than 3% of the intensity of the dominant peak with $m/z = 31$. This fact allows one to conclude that the most efficient fragmentation channels of $C_2H_6O_2$ molecules are those with the formation of ions with $m/z = 31$ and 33. At the electron energy $E_i = 70$ eV, the intensity of the peaks corresponding to different ion-fragments grows (see Fig. 1,c). An increase in the internal energy of a molecular ion leads to the complication of the mass spectrum and the appearance of fragments formed both due to its direct decay and the dissociation of primary fragments with excess energies, i.e. the secondary dissociation. It is worth noting that this mass spectrum (Fig. 1,c) is similar to the standard NIST one [11].

Let us discuss the fragmentation process in more details. As is known [12], the character of the fragmentation of alcohols under the action of electrons is determined by the localization of a cation-radical center at a heteroatom. The presence of a hydroxyl group results in a decrease of the ionization energy of such compounds as compared with that of alkanes with the same length of the carbon skeleton. In this case, the intensity of the peak of a molecular ion M^+ decreases (for example, one can compare the ionization energies of M^+ for ethane ($E_i = (11.52 \pm 0.04)$ eV), ethanol ($E_i = (10.48 \pm 0.07)$ eV), and ethylene glycol ($E_i = 10.16$ eV) [11].
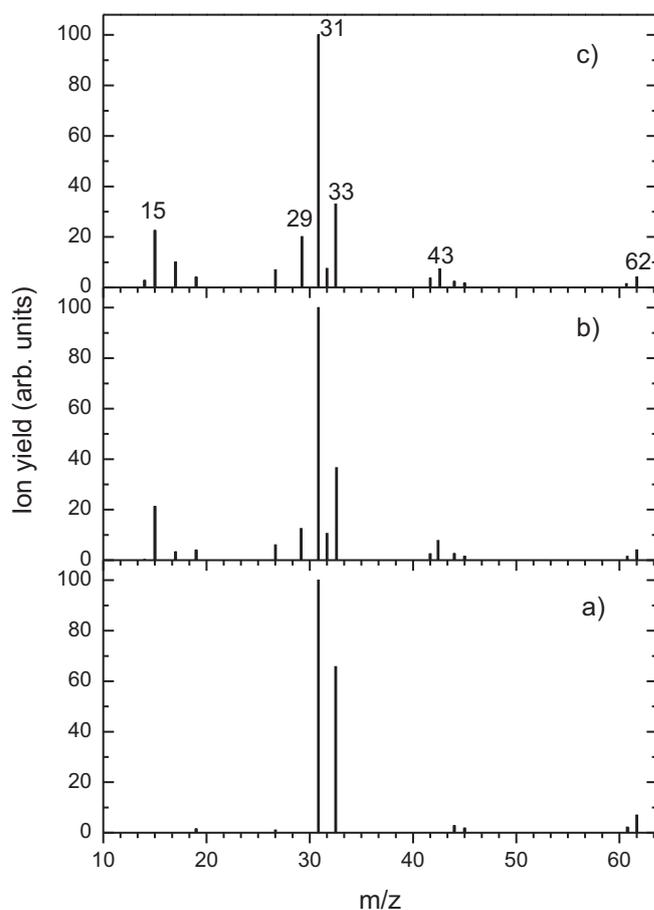

Fig. 1. Mass spectra of ethylene glycol molecules at ionizing electron energies of 30 (a), 50 (b), and 70 eV (c). The temperature of the molecule source is 350 K

We measured the appearance energies (E_{ap}) of basic ions formed due to the dissociative ionization of ethylene glycol molecules with the mass-to-charge ratios m/z=62, 44, 43, 33, 31, and 29 that are listed in Table 1. Figure 2 presents the dissociative ionization functions for the basic fragments of a studied molecule. They were used to determine the appearance energies of the given fragments with the help of the technique developed and proposed in [16].

Let us consider possible schemes of the formation of basic fragments of ethylene glycol molecule under the action of the electron impact, as well as the experimentally determined energies of their appearance in the spectrum.

Region of molecular ion with $m/z = 62$. In the mass spectrum of ethylene glycol measured at an ionizing electron energy of 50 eV (Fig. 1,b), the intensity of the peak corresponding to a molecular ion M^+ ($C_2H_6O_2^+$, $m/z = 62$) is very weak and amounts to only 4% of the most

T a b l e 1. **Brief description of fragments of ethylene glycol molecule in the mass spectrum**

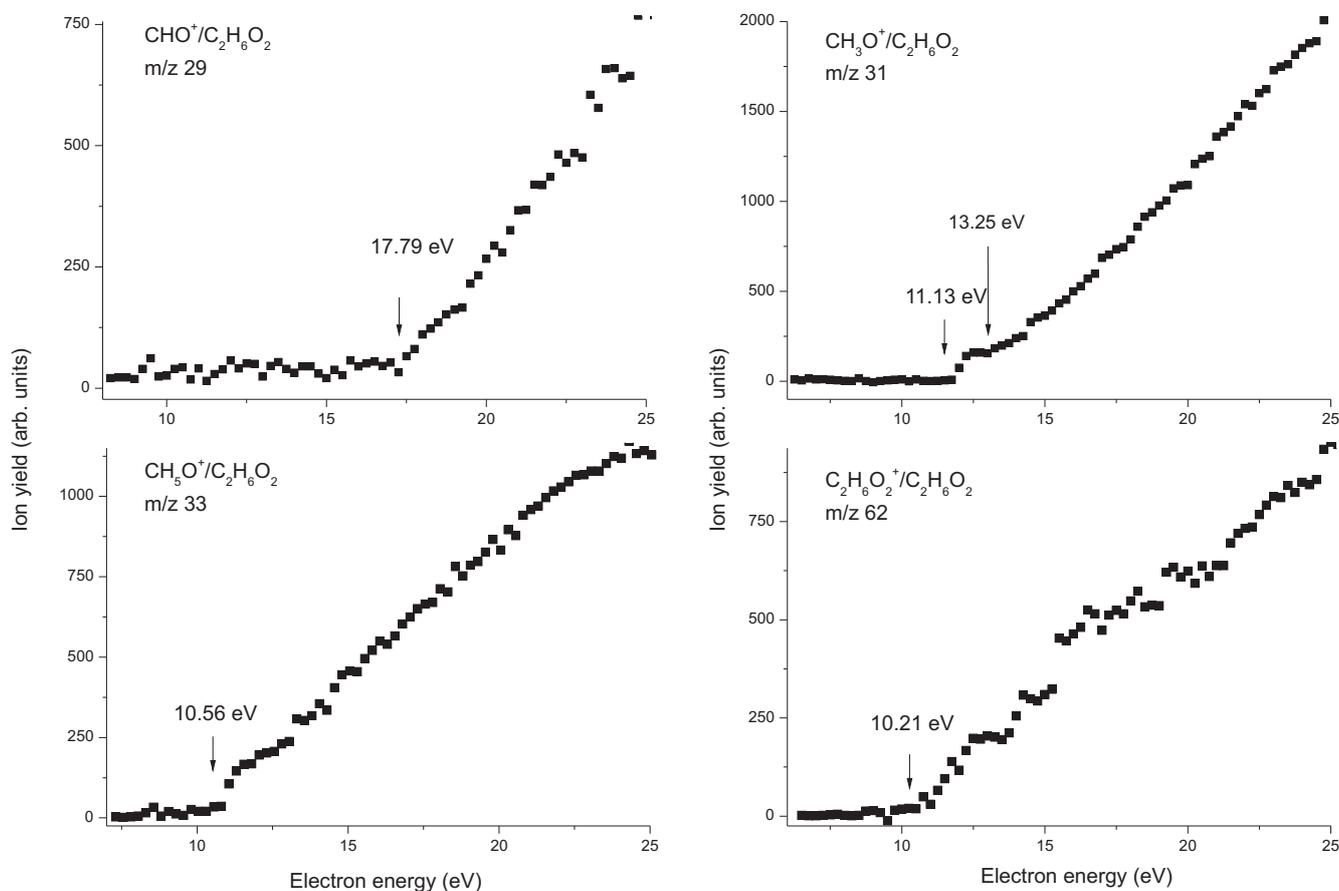| Empirical formula of the fragment ion	Molecular mass of the fragment ion, m/z	Relative intensity in the spectrum, %, at $E_i = 50$ eV	E_{ap}, eV (our data)	E_{ap}, eV NIST [11]
CH_3^+	15	22.5	16.04 ± 0.25	
CHO^+	29	13.4	17.79 ± 0.25	
CH_3O^+	31	100	13.25 ± 0.25	12.5 ± 0.15
			11.13 ± 0.25	11.12 ± 0.05
CH_5O^+	33	36.6	10.56 ± 0.25	10.7 ± 0.1
$C_2H_3O^+$	43	9.3	12.17 ± 0.25	
$C_2H_4O^+$	44	3.4	15.49 ± 0.25	
$C_2H_5O^+$	45	5.9	12.41 ± 0.25	
$C_2H_6O_2^+$	62	4	10.21 ± 0.25	

Fig. 2. Ionization efficiency curves for molecular and fragment ions of ethylene glycol molecule in the near-threshold energy region (arrows mark their energies of appearance)

intense peak in the mass spectrum belonging to CH_3O^+ ion with $m/z = 31$. Such a weak intensity of the M^+ peak is caused by its instability resulting in its dissociation. It is known that the first ionization potential of alcohol molecules is due to the elimination of the n-electron of an oxygen atom [17]. That is, the instability of the $M^{+\cdot}$ ion of ethylene glycol resulting in the low intensity of this peak in the mass spectrum is induced

by the fragmentation processes initiated by the ionized hydroxyl group. According to our calculations, the ionization energy of ethylene glycol molecule amounts to (10.21 ± 0.25) eV (see Table 1). It is worth noting that, in the case of alcohols, the formation of an intermolecular hydrogen bond can lead to the appearance of MH^+ ion peaks in the mass spectrum [17], whose intensity exceeds that of the first isotope peak $[M+1]^+$. We did not

observe MH^+ ions in our spectra, so the intermolecular hydrogen bond has no effect on the results obtained under our experimental conditions. The fragment with $m/z = 61$ corresponds to the detachment of a hydrogen atom from the molecular ion. The weak intensity of the signal from this ion in the mass spectrum does not allow us to determine the energy of its appearance.

Group of ions with $m/z = 43, 44,$ and 45. This group of fragments in the spectrum corresponds to the important decay channel of ethylene glycol molecular ion consisting in the elimination of a water molecule and hydroxyl: $[M–H_2O]^+$, $m/z = 44$; $[M–OH]^+$, $m/z = 45$. The elimination of the water molecule can be accompanied by the capture of hydrogen ($[M–H_2O–H]^+$, $m/z = 43$) [13]. Moreover, a hydrogen atom can be captured from various positions, which is considered as the transformation of $M^{+\cdot}$ preceding its decay [11]. We determined the energies of appearance of the ion-fragments $[C_2H_3O]^+$ and $[C_2H_4O]^+$ that amounted to $E_{ap} = (12.17 \pm 0.25)$ eV ($m/z = 43$) and $E_{ap} = (15.49 \pm 0.25)$ eV ($m/z = 44$), respectively. The fragment with $m/z = 45$, associated with the detachment of a hydroxyl group from the molecular ion, has a low-intensity signal in the mass spectrum, which does not allow us to determine the energy of its appearance. The peak of $[C_2H_3O]^+$ ion, that corresponds to the detachment of $[H_2O + H^{\cdot}]^+$ from the parent molecule, has the highest intensity and the least appearance threshold in this group of ions. Thus, the simple bond breakage between a carbon atom and a hydroxyl group in an ethylene glycol molecule represents a less probable fragmentation channel as compared with a more complex process accompanied by a shift of hydrogen atoms to the cation center of the molecular ion. This phenomenon can be related to the stability of generated dissociation products. To our mind, the lower value of E_{ap} in this group of ions corresponds to the formation of a relatively stable hydronium radical $H_3O^{\cdot}$, whereas the larger one is related to the detachment of two radicals $H^{\cdot}$ and $OH^{\cdot}$ from the initial molecule, rather than to the formation of H_2O.

CH_5O^+ ($m/z = 33$). The identification of the peak with this integer mass meets some difficulties, as there exist two isobar ions that can originate from the initial molecule. They are a hydroperoxide radical $[HO_2]^+$ with a molecular mass of 33.0067 amu and a protonated methanol ion $[CH_5O]^+$ with a mass of 33.0493 amu [11]. A peak of the ion of such a composition with a lifetime of 10^{-11} s was registered at the dissociative ionization of an isobutanol molecule in [15] and was identified as a protonated methanol ion. The empirical formula of the ion with m/z 33 can be determined, by analyzing
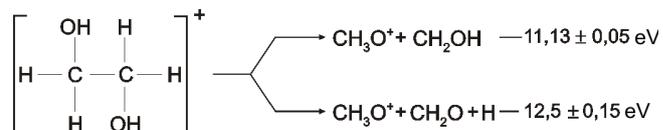

Fig. 3. Fragmentation scheme of the molecular ion of ethylene glycol molecule

its first isotope peak. Summing the increments of the intensities of the isotope peaks belonging to atoms that enter the both compounds, one calculated the intensity of the first isotope peak ($m/z = 34$) that amounted to 1.6% for CH_5O and 0.816% for HO_2. The intensities of the peaks with masses of 33 and 34 in the spectrum [11] relate as 100:1.4, i.e. the ion with a mass of 33 amu in the ethylene glycol spectrum has the empirical formula $[CH_5O]^+$ accurate to $\pm$ 0.1%. Thus, the presence of the peak with $m/z = 33$ $[CH_5O]^+$ and the energy of appearance $E_{ap} = (10.56 \pm 0.25)$ eV in the spectrum is a result of the breakage of the C–C bond of the carbon skeleton of a molecule, as well as the rearrangement and the migration of hydrogen atoms.

CH_3O^+ ($m/z = 31$). The peak corresponding to this mass is the most intense in the spectrum. The formation of oxonium ion $CH_2{=}\overset{\bullet\bullet}{\underset{+}{O}}H$ ($m/z = 31$) represents the main dissociative process in the case of the fragmentation of all aliphatic alcohols [12], including ethylene glycol, and corresponds to the β-breakage of the C–C bond (with respect to a heteroatom), which can be a result of the charge localization at an oxygen atom. The energy of appearance of the ion corresponding to this mass is $E_{ap} = (11.13 \pm 0.25)$ eV. In the case of ethylene glycol, the dissociation of this bond can occur through two channels with the formation of various products (see Fig. 3), which is reflected in the break of the ionization efficiency curve for CH_3O^+ ion, and, respectively, different thresholds of its appearance.

CHO^+ ($m/z = 29$). The peak of CHO^+ ion with $m/z = 29$ corresponds to the loss of a fragment (fragments) with a mass of 33 amu by the molecular ion. Moreover, either the whole CH_5O fragment or its separate parts (e.g., $CH_3 + H_2O$, $CH_2 + H_3O$) can be eliminated, which is manifested in the nonuniformity of the ionization efficiency function at the formation of CHO^+ ion. The energy of appearance of this ion is equal to (17.79 ± 0.25) eV. With regard for the fact that the formation of the majority of fragments requires a higher energy consumption, the appearance threshold of this ion corresponds to the detachment of the CH_5O fragment, i.e. CHO^+ ion is complementary to CH_5O^+ one with $m/z = 33$. Since E_{ap} for CH_5O^+ is much lower
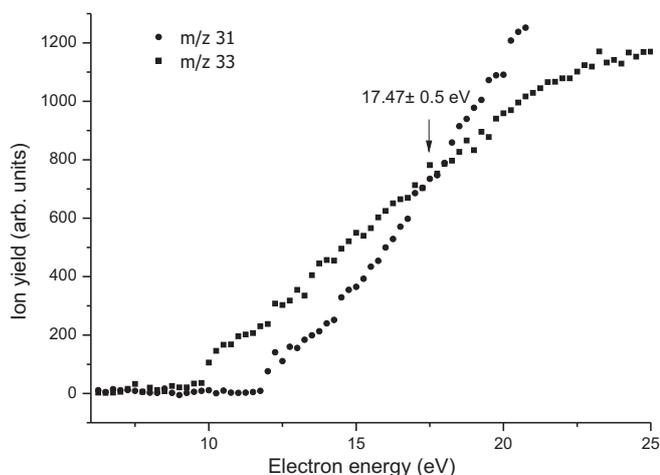
Fig. 4. Near-threshold regions of the ionization efficiency functions for CH_5O^+ ($m/z =31$) and CH_3O^+ ($m/z =33$) ions

as compared with E_{ap} for CHO^+ (see Table 1), whereas the energies spent for the bond breakage and a rearrangement of atoms at the formation of complementary fragments are identical, the difference in the energies of appearance of these ions corresponds to the difference in the ionization energies of the respective fragments and amounts to (7.23 ± 0.5) eV. The relation between the peaks of these ions in the mass spectrum also testifies to the better charge stabilization by an ion with larger mass.

CH_3^+, ($m/z = 15$) . In the case of the electron impact fragmentation of aliphatic alcohols, the dehydration of not only M^+, but also of fragment ions including a hydroxyl group, can occur. To our mind, it is the process that results in the appearance of the peak with $m/z = 15$ (CH_3^+) in the ethylene glycol spectrum that is most probably formed due to the dehydration of CH_5O^+ fragment ion. The ion corresponding to this mass has the energy of appearance $E_{ap} = (16.04 \pm 0.25)$ eV.

Interesting features can be observed in the behavior of the near-threshold regions of the ionization efficiency functions for CH_5O^+ and CH_3O^+ ions (Fig. 4), whose peaks dominate in the mass spectra at ionizing electron energies of 30–70 eV (Fig. 1). The values of E_{ap} for these ions are equal to (10.56 ± 0.25) and (11.13 ± 0.25) eV, respectively. In other words, a simple breakage of the C–C bond with the formation of CH_3O^+ ion-fragment at a low level of the excess energy of a molecular ion appears less energy-advantageous than the complex process of rearrangement of hydrogen atoms and the dissociation of the same bond under formation of CH_5O^+ ion-fragment. The increase in the internal excess energy of the molecular ion leads to the redistribution of com-

peting fragmentation channels. At 17.47 eV, a simple breakage of the C–C bond without atom rearrangement becomes the prevailing channel of dissociative ionization of the studied molecule.

4. Conclusions

The present work reports the results of complex mass spectrometric studies of the processes of electron impact dissociative ionization of ethylene glycol molecules. They give a possibility to deeper understand the mechanisms of interaction of slow electrons with these molecules. For the majority of fragment ions, we propose possible ways of their formation and determine their energies of appearance.

A general regularity of the dissociative ionization of ethylene glycol molecule (similar to those observed for methanol, ethanol, and butanol molecules in our previous studies [8]) consists in the presence of CH_3^+ and CH_3O^+ ion fragments. However, there exist certain differences. In particular, comparing the intensities of the peaks belonging to ions with $m/z = 43$ - 45 in the mass spectrum with the obtained appearance thresholds of these fragments allowed us to make conclusion that such simple channel of fragmentation of a molecular ion as the detachment of a hydroxyl group is inefficient for the majority of alcohols. Instead, the ethylene glycol molecular ion experiences a more complex process accompanied by a shift of hydrogen atoms to the cation center of this ion.

Another peculiarity is that, at ionizing electron energies from the threshold to (17.47 ± 0.50) eV, one can observe the predissociative rearrangement processes in a molecular ion, and the main channel of its dissociation is the formation of CH_5O^+ ion and the CHO neutral fragment. An increase of the electron kinetic energy results in the inversion of channels leading to the appearance of CH_3O^+ and CH_5O^+ ions that have the most intense peaks in the mass spectrum. Thus, a simple breakage of the C—C bond with the formation of CH_3O^+ ion fragment becomes the dominant fragmentation channel of a $C_2H_6O_2$ molecule.

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ІОНІЗАЦІЯ МОЛЕКУЛИ ЕТИЛЕНГЛІКОЛЮ ЕЛЕКТРОННИМ УДАРОМ

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Р е з ю м е

Проведено мас-спектрометричні дослідження виходу позитивних іонів, утворених внаслідок іонізації електронним ударом молекули етиленгліколю в газовій фазі. З кривих ефективності іонізації отримано енергію іонізації молекули і енергії появи основних фрагментних іонів. Експериментально визначено значення енергії іонізації для молекули $C_2H_6O_2$, яке становить $10,21 \pm 0,25$ eB. Для основних фрагментних іонів з $m/z = 31$, 33 і 29 експериментально знайдені значення енергій появи становлять $11,13 \pm 0,25$, $10,56 \pm 0,25$ і $17,79 \pm 0,25$ eB відповідно.