FORMATION OF SLOW IONS WHEN FAST PROTONS AND HYDROGEN ATOMS PASS THROUGH NITROUS OXIDE

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A study was undertaken of the mass spectra of slow ions, formed in the processes of dissociative ionization of the N_2O molecule by fast protons and hydrogen atoms, and of the mass spectra of slow negative ions formed in the processes of charge exchange between the hydrogen atom and the N_2O molecule. A comparison was made of the relative intensities of beams of slow ions with the energies needed to break the bonds in the N_2O molecule.

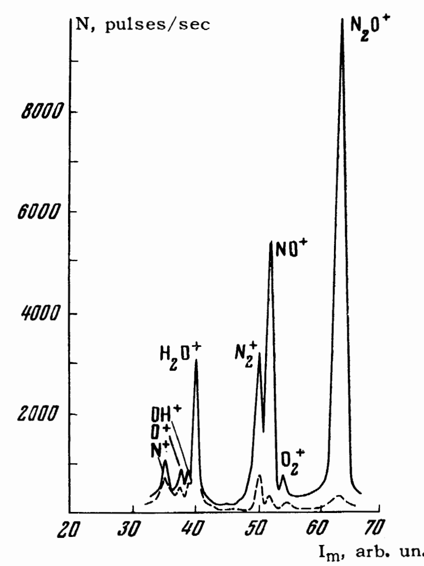
IN our earlier investigations,[1,2] we used a double mass-spectrometer apparatus to study the processes of formation of slow positive and negative ions in the collisions of fast atoms and negative ions of hydrogen with the molecules of a number of diatomic gases. The investigation reported here was carried out on the triatomic gas molecule N_2O (nitrous oxide).

The sensitivity of the apparatus was considerably increased (by about two orders of magnitude) by replacing the system used to detect slow ions at the output of the mass spectrometer. Instead of the arrangement consisting of a secondary-electron multiplier and electrometer amplifier at the mass-spectrometer output, we used an ion counter, with a noise level of 3—5 pulses in 10 sec, which has been described by Kozlov et al.[3]

The nitrous oxide was prepared by the thermal decomposition of ammonium nitrate NH_4NO_3. Special mass-spectrometric and spectroscopic investigations showed that the nitrous oxide did not contain N_2 as an impurity. The investigations were carried out at an N_2O pressure of the order of 10^{-4} mm Hg. The residual gas pressure in the collision chamber amounted to $(3-5) \times 10^{-5}$ mm Hg.

The mass spectra of slow positive and negative ions were obtained by passing, through the N_2O, hydrogen atoms having energies of 8 and 30 keV. We also obtained the mass spectrum of slow positive ions formed by passing through the N_2O a beam of protons of 30 keV energy. The figure gives the mass spectrum of slow positive ions, obtained by passing through the N_2O hydrogen atoms of 8 keV.

It is evident from the figure that the mass spectrum of positive ions included the ions N_2O^+, NO^+, N_2^+, O^+, and N^+ (which are listed in decreasing order of their intensity), formed as a result of nondissociative and dissociative ionization and charge-exchange processes in the collisions of the hydrogen atoms with N_2O molecules. The N_2O^+ ion produced by these processes may decay as follows:



Spectra of slow positive ions (E_{H^0} = 8 keV): continuous line represents the spectrum of the investigated gas, and the dashed line is the residual gas spectrum.

$$N_2O^+ \rightarrow NO^+ + N, \quad (1a)$$

$$N_2O^+ \rightarrow NO + N^+; \quad (1b)$$

$$N_2O^+ \rightarrow N_2^+ + O, \quad (2a)$$

$$N_2O^+ \rightarrow N_2 + O^+. \quad (2b)$$

From the relative intensities of the mass lines in the spectrum given in the figure, we can draw the following conclusions:

1) The probabilities of formation of stable and unstable N_2O^+ ions in the collisions of hydrogen atoms with N_2O molecules are of the same order of magnitude.

2) The probability of decay of unstable N_2O^+ ion involving the breaking of the N—NO bond [process (1)] is considerably higher than the probability of decay involving the breaking of the N_2—O bond [process (2)].

3) The probabilities of the processes (1a) and (2a) are considerably higher than the probability of processes (1b) and (2b), i.e., the N_2O^+ ion decays mainly to form molecular charged fragments.

A comparison of the spectra of positive ions formed in N_2O by protons and hydrogen atoms of 30 keV energy leads to the conclusion that the charge state of a fast particle has very little influence on the relative intensities of the mass lines. This is evidently associated with the fact that the formation of N_2O^+ ions is mainly due to the ionization of N_2O molecules by the impact of fast particles and not to the charge-exchange processes.

We found some dependence of the relative intensities of the mass lines in the spectrum of positive ions on the fast-particle velocity. In particular, as the velocity of the hydrogen atom decreased, the probability of process (1a) increased and the probability of process (1b) decreased.

We found only the O^- ions in the spectrum of the slow negative ions, formed in the collisions of 8 and 30 keV hydrogen atoms with N_2O molecules. Hence, we can draw the following conclusions:

a) N_2O^- ions are not formed in the collisions of hydrogen atom with N_2O molecules. In this respect, the N_2O molecule differs from the NO molecule, for which collisions with hydrogen atoms give rise mainly to NO ions.[1] This difference is evidently associated with the fact that the N_2O^- ion is unstable.

b) The decay of the unstable ion N_2O^-, formed in the charge exchange of the hydrogen atom with the N_2O molecule, involves the breaking of the N_2—O bond. NO^- ions, which can be formed from N_2O^- ions by breaking the N—O bond, are not observed.

The mass spectrum of ions formed in the collisions of electrons with N_2O molecules has been investigated in[4-6] (positive ions) and in[7-9] (negative ions). The mass spectrum of positive ions, formed by electron collisions with N_2O molecules, is characterized by a low probability of the process (2a) compared with the probability of the process (1a), which follows from the results given in[6], whose authors did not detect N_2^+ ions in the mass spectrum. Although other workers[4,5] have reported the presence of N_2^+ ions in the mass spectrum, they have themselves pointed out that the investigated nitrous oxide contained a considerable amount of nitrogen impurity and this accounted for the appearance of N_2^+ ions in the mass spectrum. The low probability of the process (2a) in the collisions of electrons with N_2O molecules has also been confirmed in[10,11], where the spectrum of the radiation of N_2O, excited by electron impact, was investigated. This spectrum had bands of the N_2O^+ and NO^+ molecules but had no bands of the first negative system of the N_2^+ molecule (this will be denoted by "1 neg. N_2^+").

Thus, we may conclude that the probability of the process (2a) in the collisions of heavy particles (H^+, H) with the N_2O molecule is considerably higher than in electron collisions. This conclusion is confirmed not only by the results of mass-spectrometric measurements, but also by the data from spectroscopic investigations carried out using the apparatus described in[12], where it was shown that the emission spectrum of N_2O, excited by the impact of protons of 30 keV energy, included the 1 neg. N_2^+ bands. The different probabilities of the process (2a) in the collisions of electrons and heavy particles with N_2O molecules may be associated with the fact that the velocity of electrons employed in the investigation reported in[6,10,11] was higher than the velocities of the protons and hydrogen atoms used in the present investigation. However, it is also possible that this difference was, to some extent, due to the different nature of the ionizing particle.

According to the data reported in[7-9], only O^- ions were observed in the mass spectrum of the negative ions formed in the collisions of electrons with N_2O molecules. It thus follows from the results of the present investigation that the nature of the mass spectra of the negative ions, formed in the collisions of electrons and hydrogen atoms with N_2O molecules, are the same. In this respect, the N_2O molecule differs considerably from the NO molecule, for which the nature of the mass spectrum of negative ions depends on the nature of the incident particle.[1,2]

In conclusion, it is interesting to compare some features of the decay of the N_2O^+ and N_2O^- ions and of the N_2O molecule.

According to the published data,[13] the energies required for breaking the N_2—O bonds and NO—N bonds are 1.2 and 4.5 eV. In accordance with these results, the thermal dissociation of the N_2O molecule involves mainly the weaker N_2—O bonds.[14] It follows from the data just presented that the same bond is broken in the dissociation of the N_2O^-

ion. The processes of dissociation of the N_2O^+ ion, formed by charge exchange between a number of positive ions with N_2O molecules, have been investigated in[15] and it has been shown that, in a considerable majority of cases, the dissociation of the N_2O^+ ion involves mainly the NO—N bond. The results of the present investigation also indicate that the breaking of the NO—N bond in N_2O^+ is more likely. However, it follows from[15] that, in some cases, the N_2—O bond is more likely to be broken. All this indicates that the probability of the formation of NO^+ and N_2^+ ions in the processes of dissociation of N_2O^+ ions depends not only on the energy required to break bonds in the N_2O^+ ion, but also on the type of process by which this ion is formed.

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