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MASS-SPECTROSCOPIC STUDY OF DISCHARGE PRODUCTS IN WATER VAPOR

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An experimental study of free radicals and atoms drawn out by a jet from a glow discharge in water vapor was carried out in a number of works (1–4). This question is of considerable importance, since a discharge in water vapor is used as a source of active particles for studying their reactions (3), and also because knowledge of the composition of the decomposition products in the discharge is important for understanding the mechanism of reactions in the discharge and, possibly, of radiation-chemical reactions.

Free hydroxyl in the products of a discharge in water vapor was detected spectroscopically (1,2), and its concentration was determined with sufficient accuracy. As for oxygen atoms, no direct spectroscopic measurements of them have been made, although in older works (5) there are some indications of the possibility of their formation. At the same time, oxygen atoms were detected by L. I. Avramenko (3) from the glow upon additions of NO and from a number of chemical indications, in concentrations considerably exceeding, under the conditions of his experiments, the concentration of free hydroxyl.

It was of interest to carry out mass-spectrometric measurements of the atoms and radicals formed during a discharge in water vapor, which was done in the present work.

The measurements were made on a mass spectrometer specially developed for determining free radicals and atoms*. A special feature of this instrument was the introduction of the analyzed mixture into the ion source in the form of a molecular beam. By periodically interrupting the beam with a shutter and measuring only the component of the mass-spectrum line intensity that changed in this process (the "modulated" component), it was possible to eliminate the "background" of the instrument and also, to a considerable extent, to avoid suppression of the spectrum of free radicals and atoms caused in mass spectrometers of the usual type by their heterogeneous destruction on the walls of the ionization chamber. The latter issue is especially important in the analysis of such particles as H, O, and OH, for which the probabilities of heterogeneous recombination on metals are large (6).

The use of a modulated molecular beam in a mass spectrometer for the analysis of free radicals was described by Foner and Hudson (7). In contrast to their design, in our instrument the molecular beam is not perpendicular to the ion beam but coaxial with it. This makes it possible to improve the ratio of the ionic signal of the molecular beam to the ion current obtained from molecules of the residual gases of the instrument and scattered particles of the analyzed mixture. Such an improvement occurs because ions obtained from particles of the molecular beam, with the slit widths used, have a much greater probability of leaving the source.

* The development of the instrument was carried out by V. L. Tal' roze, L. L. Dekabrun, G. D. Tantsyrev, and A. K. Lyubimova (part of the electronic units of the instrument is described in (8,14)).

The system for forming the molecular beam and the connection diagram of the discharge setup with the mass spectrometer are shown in Fig. 1. The molecular beam was formed by the inlet diaphragm 5 and by the narrow channel 6 (the channel consisted of two parts: a narrow one, $d = 0.15$ mm, $l = 3$ mm, and a wider one, $d = 0.6$ mm, $l = 13$ mm). Between them was placed shutter 7, which modulated the beam; it was attached to a sylphon and could be moved by hand or by means of an electromagnetic relay. The pressure in volume 8 was 10^{-3}—10^{-4} mm Hg. (The distance between the inlet diaphragm and the channel was 7 mm, and between the outlet opening of the channel and the ion source, 30 mm.)

(Figure: Fig. 1. Schematic of the apparatus)

Fig. 1. Schematic of the apparatus

The inlet diaphragm was a Pyrex cap with a flat bottom about $30\,\mu$ thick and with an aperture $d \sim 150\,\mu$. The technique for manufacturing such diaphragms is described in (9). The Pyrex tube B with the diaphragm was vacuum-tightly attached to flange 1, which through sylphon 3 was connected to pumping tube 4. By means of screws n and m, flange 1 could be moved relative to flange 2 along a ground surface, making it possible to adjust the system. The distance between the discharge tube and the diaphragm was 300 mm. Water vapor entered the discharge tube from a flask with stopcock K and was drawn through tube A and trap L, cooled with liquid nitrogen, which, under conditions of a low degree of water decomposition in the discharge, served as a powerful pump. The pressure was measured at points a, b, and c with a U-shaped oil manometer and was regulated by stopcock K and by the temperature of the water bath in which the flask with water was placed. The walls of the discharge tube and tube A were treated with concentrated metaphosphoric acid.

1. Calibration of the mass spectrometer for H and O atoms. The instrument was calibrated for H and O atoms obtained by drawing hydrogen or oxygen, respectively, through the discharge. The number of atoms in the flow was determined from the amount of heat released upon their recombination on a platinum spiral placed between tubes A and B at a distance of 5 mm from the diaphragm (wire diameter 0.1 mm; the spiral was fastened to thin glass whiskers sealed to the outer surface of tube A). The spiral was included in a bridge measuring circuit. The heat released on the wire as a result of atomic recombination when the discharge was switched on was compensated by changing the heating power of the wire so that the temperature of the wire (i.e., its resistance) remained constant.

A necessary condition in such measurements is the recombination of all atoms. To check the fulfillment of this condition, a second spiral was installed behind the Pt spiral at a short distance from it. The amount of heat released on the second spiral was 10—15 times less than on the first.

the first. This made it possible to conclude that on the first spiral $\sim 90\%$ of all atoms recombine.

The atom concentration was found in calibration experiments to be equal to 30% both for H atoms and for O atoms. Along with measuring the atom concentration in the jet, the modulated components of the ion currents were measured with the discharge switched on (I') and switched off (I''). The values I', I'', and $I' - I''$ are given in Table 1. The pressure in this experiment was 0.8_2 mm Hg.

The ion current due to the atoms themselves, in the case of H atoms, is

$$I_H = (I' - I'')_{m/e=1} K_{\mathrm{H2}} (I' - I'')_{m/e=2},$$

where K_{H2} is the ratio of the intensities of the line at 1 a.m.u. to the line at 2 a.m.u. in the mass spectrum of H_2, determined with the discharge switched off. The magnitude of the ion current for O atoms is determined analogously.

Table 1

m/e	Hydrogen, electron energy 66 V	m/e	Oxygen, electron energy 30 V				
	I' mm of scale	I''	$I' - I''$ mm of scale		I'	I''	$I' - I''$
1	41	21	20	16	280	190	90
2	460	534	−74	32	210	360	150

The sensitivities of the instrument η, defined as the ratios of the partial pressures of the atoms to the corresponding ion current I, are equal to

$$\eta_H = 1.25 \cdot 10^{-2} \, \frac{\text{mm Hg}}{\text{mm of scale}}, \qquad \eta_O = 2.7 \cdot 10^{-3} \, \frac{\text{mm Hg}}{\text{mm of scale}}.$$

For such a calibration to be valid, it is essential that proportionality between the pressure in tube *A* and the ion current be maintained over the entire range of working pressures.

(Figure: Fig. 2)

Fig. 2. Dependence of the intensity of the $m/e = 16$ line in the mass spectrum of O_2 on the pressure before the inlet diaphragm.

Figure 2 shows the calibration of the instrument with respect to O_2 pressure for the $m/e = 16$ line. As is seen from Fig. 2, direct proportionality is maintained up to a pressure of 6 mm Hg.

2. Results of mass-spectrometric measurements of the concentration of atoms and radicals in the products of discharge in water vapor. Measurements were carried out at pressures of 0.5–4 mm Hg and a current in the discharge of 100–150 mA. The intensities of the ion currents I' and I'' were measured for $m/e = 1;\ 2;\ 16;\ 17;\ 18$ and 32.

At a water-vapor pressure in the discharge of 0.5–1.5 mm Hg, it was possible to observe H atoms and free hydroxyl, but O atoms could not be found. An estimate from the sensitivity of the instrument showed that the concentration of O atoms in any case was less than the concentration of OH.

When the pressure was increased to 3 mm Hg, O atoms were detected. The results of measurements of the concentrations of H and O atoms and free hydroxyl are given in Table 2 (the jet velocity was 30 m/s, the degree of conversion of water was 3–4%).

Table 2

m/e	I'	I''	$I' - I''$	I	Electron energy, V
	in scale units				
1	80	65	15	5	66
2	60	0	60		66
16	51	16	35	23	30
17	288	250	38	10	30

The ion-current values I in Table 2 are determined only by H and O atoms and free hydroxyl. They were obtained by subtracting from the values $I' - I''$ for the lines $m/e = 1$; 16, and 17 the corresponding values due to dissociative ionization of H_2, H_2O, and O_2 (the value K_{H_2O} was found in a separate experiment).

The concentrations of H and O atoms and free hydroxyl, obtained by multiplying the values of I by the corresponding sensitivity coefficients,

were found to be: [H] = 0.06 mm Hg, [O] = 0.06 mm Hg, [OH] = 0.03 mm Hg. These values were determined to within a factor of 1.5–2. The concentration of O_2 was 0.04 mm Hg, i.e., it was less than the concentration of O atoms*. In calculating the value of [OH] we assumed that $\eta_0 = \eta_{OH}$. Such an assumption is valid, at least to an accuracy of 20-30%, since the numbers of electrons in these particles differ by only 12%, and the intensity of line 16 in the mass spectrum of free hydroxyl, even at 70 eV (10), does not exceed 25% of the intensity of line 17. (That the intensity of line 16 in the mass spectrum of OH is less than that of line 17 is also indicated by our experiments at low pressures, in which OH was detected from the excess intensity of line 17, but no excess intensity of line 16 was detected.)

Thus, mass-spectrometric measurements confirm the presence, among the products of a discharge in water vapor, of a significant concentration of O atoms. The question arises as to the mechanism of their formation in the discharge.

From the recently established fact that there is no activation energy in ion-molecule reactions (11–12), it follows that at least two processes must lead to the formation of O atoms in the discharge:

$$\mathrm{OH}^{+} + \mathrm{H_2O} \to \mathrm{O} + \mathrm{H_3O^{+}} + 58\ \mathrm{kcal/mol};$$

$$\mathrm{OH} + \mathrm{H_2O^{+}} \to \mathrm{O} + \mathrm{H_3O^{+}} + 47\ \mathrm{kcal/mol}.$$

At elevated pressure these processes should play an increasingly important role. It is possible that the previously held view that O atoms constitute only a small fraction of the discharge products in water vapor was connected precisely with this; that view was based on experiments carried out at low pressures (tenths of a millimeter Hg) and was in contradiction with Avramenko' s experiments, carried out at a pressure of several millimeters Hg. This interpretation also agrees with the fact that O atoms were not detected by us in the region of lower pressures.

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* O_3 and H_2O_2 were not detected in the mass spectrum.

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

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