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EFFICIENT OZONE GENERATOR FOR OZONE LAYER ENRICHMENT FROM HIGH ALTITUDE BALLOON.

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ABSTRACT

The possibilities of ozone production at low gas pressures by nanosecond high voltage discharge has been investigated. The measurements of ozone synthesis in N_2-O_2 mixtures have been performed. The explanation of experimental results is suggested. The possible ways of ozone yield growth are analyzed.

1.INTRODUCTION

An enrichment of ozone layer hole by generators placed on the high altitude balloon is one of possible way of its efficient restoration. The ozone generators planned to utilize for these purposes should be adjusted according to the following demands: 1.They should efficiency operate at low pressure corresponding to one's in ozone layer (10-30 Torr); 2.They should produce ozone in natural concentration which is not more than $10^{13}cm^{-3}$. The production of ozone in much more concentration is unless because its efficiency destruction by UV light. 3.Disturbances of gas parameters must be unsufficient. 4.The production of impurities, efficiently destroying ozone layer such as NO, etc. must be seriously restricted.

The efficiency of planned ozone generator must be extremely high. The ozone generators utilizing MW-discharge, corona discharge (impulse and stationary) efficiency operate at gas pressure about 100 Torr and more. A serious restriction of utilizing these types of ozone generators for ozone layer enrichment is in nitrogen oxides production in the significant concentrations.

Also it should be mentioned that only laboratory simulation of ozone kinetics at conditions corresponding to that of in ozone layer are now available because of the difficulties of its reproducing at above means of gas excitation. So the problem of experimental modeling of the ozone layer chemistry at natural conditions is also of great importance.

A breakdown of gas in the form of the sub-light velocity breakdown ionization wave (BIW) propagating through the gas with 10^8-10^9cm/s velocities (Asinovsky et al., 1983; Loeb, 1965) has some attractive properties permitting to use its afterglow for effective ozone generating. An important property of the BIW which is due to the high redused electrical field strength in the BIW front (E/N≥100Td) is an effective electronics and vibrational degrees of freedom excitation of the particles with negligible heating of the gas. So, strongly nonequilibrated, cold plasma with excellent spatial uniformity may be prodused in the discharge at wide pressure range (0,1-100 Torr). This feature of the BIWs permit to use them both for production of ozone at low gas pressure and for ozone layer kinetics modeling in wide range of plasma parameters variation corresponding to possible natural conditions in ozone layer of the Earth atmosphere.

In the present study we have investigated possibilities of using electric discharge in the special form of breakdown ionization wave for efficient ozone production from high-altitude balloons and for laboratory simulation of ozone layer chemistry. The ozone synthesis have been performed in BIW's afterglow in O_2-N_2 mixtures in pressure range of 5-40 Torr and reveals the high efficiency of ozone production and so possibilities of practical utilizing this type of generator for ozone layer enrichment from high altitude balloon.

2.EXPERIMENTAL FACILITIES

The experimental setup layout is shown in Fig.1. A quartz discharge tube (1) of 20 cm length and 4,65 cm inner diameter with the plate stainless steel

1- quartz discharge tube;
2- electrodes;
3- nanosecond voltage generator;
4- metallic screen;
5,6- current shunts;
7- oscilloscope;
8- UV-lamp; 9- monochromator;
10- photomultiplier;
11- bandpass filter;
12- low frequency electrical filter;
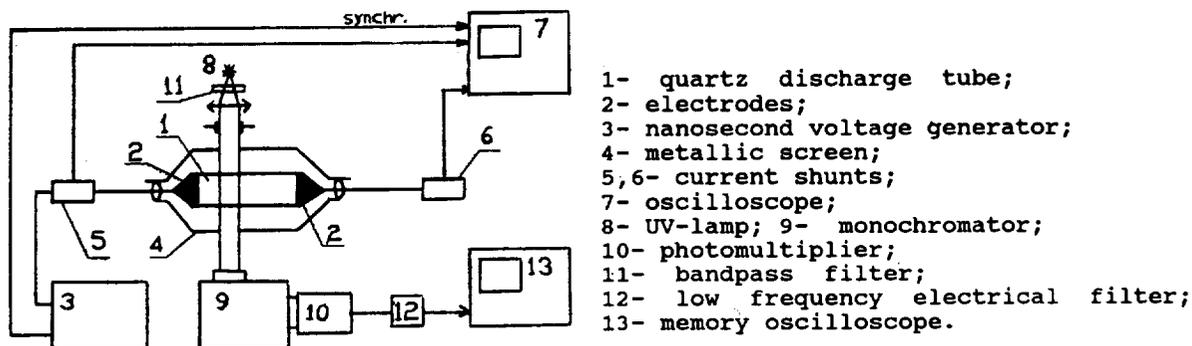13- memory oscilloscope.

Fig.1. The layout of experimental setup.

electrodes at the ends (2) is inserted into the gap of the central wire of the coaxial electrical cable connected with nanosecond voltage generator (3). The coaxial metallic screen (4) surrounding the tube is connected to the screen. The impedance of such system in assumption that the gas gap has an ideal conductivity is equal to the coaxial cable one's (Z=50 Ohm). Positive and negative polarity voltage pulses with U=15-20 kV altitude, 25 ns duration, 8 ns rise time and f=20-90 Hz repetition frequency have been used to initialize the BIW developing. The temporal behavior of the supplied to and reflected from the discharge tube electric pulses is monitored with the aid of the calibrated current shunt mounted on the outer shielding conductor of power cable before (5) and after (6) the tube. The signals from the gauges are registered by oscilloscope (7) with 1 GHz transmittance band.

The ozone concentration is measured with accuracy the order of the 10% by using absorption technique at spectral region 250±5 nm corresponding to the intensive Hartley's band of O_3. The radiation of the highly stable UV-lamp (8) passes across the discharge tube perpendicularly to its axis, than selected by monochromator (9) and registered by photomultiplier (10). To avoid the ozone formation as a result of photochemical processes in the ambient air the bandpass filter (11) with λ=250±9 nm is used. To prevent the high frequency interferences noise in the electric circuit the pulse signals from the multiplier are transmitted through low frequency electrical filter (12). This restricts resolution time of the scheme by value of 2s acceptable for our work. The resulting signal is than recorded by memory oscilloscope (13).

3. EXPERIMENTAL RESULTS

The typical oscillograms of the ozone concentration with time of repetitive discharge operation are represented in Fig.2A-D. The temporal dependence of the ozone formation on the gas pressure has two peculiarities for all investigated gas mixtures. Namely, at gas pressures P≤20-25 Torr the ozone concentration increases with time while nanosecond generator is turned on up to some value and than remain constant till generator is turned off (Fig.2A). At more high pressure P≥25-30 Torr ozone concentration has maximum and then slowly drops to the quasistationary value during some tens of seconds (see Fig.2B).

Fig.2C-D represent behavior of ozone concentration after nanosecond generator is turned off. Ozone concentration in O_2-N_2 mixtures decreases to zero (Fig.2C). In technical pure oxygen decreases to some constant value and then drops very slowly to zero (see Fig.2D).

The values of the absolute ozone concentration vs gas pressure are represented for different gas mixtures in Fig.3. The maximal values of ozone
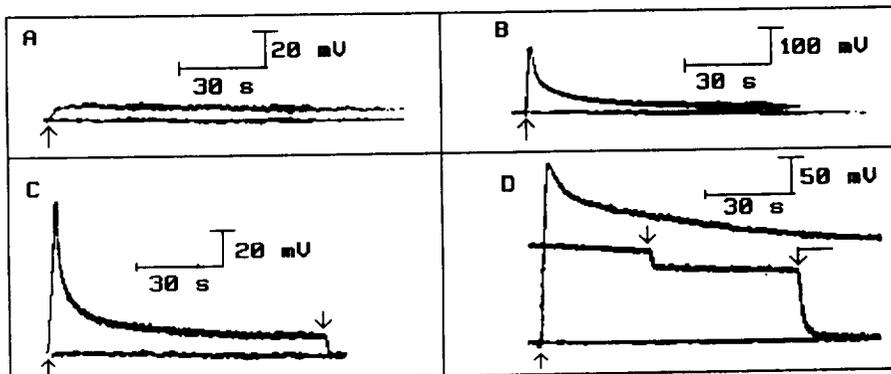
Fig.2. The typical ocsillograms from the photomultiplier. Repetition frequency f=42 Hz, negative polarity. ↑- discharge turned on; ↓- discharge turned off; √- - pumping of the discharge tube. (A): 16,2 Torr, 70,5% O_2 mixture; (B): 34,1 Torr, 70,5% O_2 mixture; (C): 30 Torr, 48% O_2 mixture; (D): 30 Torr, technical pure O_2.

concentration $[O_3]_{max}$ for all mixtures continuously increases with gas pressure (Fig.3A) to an excellent relative value $\xi=[O_3]/[O_2]$ =0,5% at highest investigated pressure P≈40 Torr in technical pure oxygen.

The maximal stationary values of ozone concentration $[O_3]_{st}$ increase in technical pure oxygen both at 42 and 82 Hz repetition frequency. The maximal relative value $\xi=0,2\%$ is achieved at 37 Torr pressure. For all investigated O_2-N_2 mixtures the dependence of stationary ozone concentration upon the pressure has slightly revealed maximum at P=20-25 Torr (Fig.3B).

Stopping energy of the gas obtained from the measurements of applied to and reflected from discharge gap electric pulses (Asinovsky, 1983), as well as ozone production efficiency (stopping energy of the gas in one pulse related to O_3 molecules at stationary concentration) also have non monotonous dependence vs pressure, with maximum at pressures P≈10-20 Torr.

4. DISCUSSION

At the present conditions we may divide the processes in the gas to some stadium:
1. Electrical pulse propagating through the gas gap, production of ions, atoms and excited particles due to high electron density and temperature $T_e \gg T_g$.

Cooling of the electron gas, radiation of short life time exited particles $(t \leq 10^{-7} s)$;
2. Recombination of ions and atoms, quenching of some metastable particles $(t \leq 10^{-4} s)$;
3. Quenching of metastable particles, vibrational recombination, chemical reactions between neutral and excited particles $(t \geq 10^{-4} s)$.

When high voltage pulse propagates through the discharge tube, high reduced electrical field is realized. Under conditions of our experiments E/N is the order of the 30÷100 V/cm·Torr. Electron temperature and concentration could reach values about some electron-volts and $n_e \approx 10^{11}-10^{12} cm^{-3}$ respectively. Under these conditions the intensive dissociation of oxygen and nitrogen take place. Produced atoms take part in chemical reactions of ozone appearance and destruction.

The main reaction of ozone production in discharge is

$$O+O_2+M \rightarrow O_3+O_2 \qquad (1)$$

This reaction is well investigated. According to many of the research, the most of O_3 molecules, created in reaction (1), are vibrationally excited. It could change velocities of ozone destruction reactions.

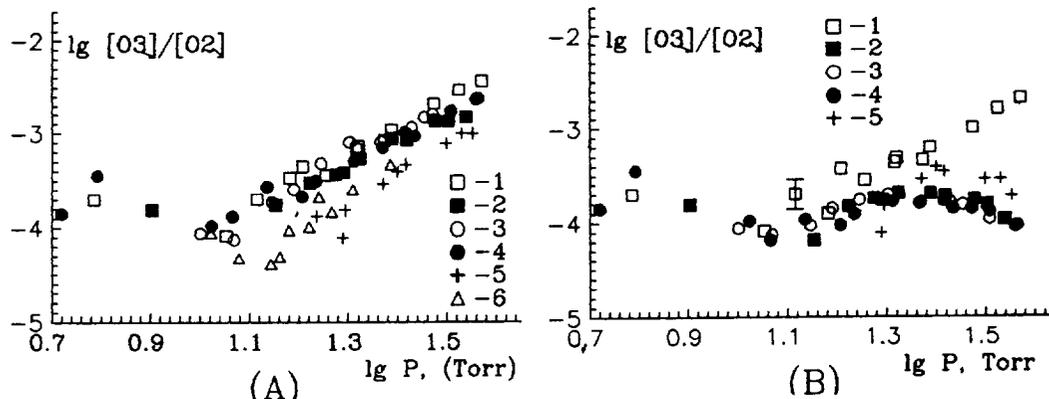Characteristic time of atoms O recombination in reaction (1) at pressure P=30 Torr and 97% O_2 mixture is

Fig.3. Ozone concentration for different mixtures as a function of gas pressure. (A)- maximal values; (B) - stationary values. 1- technical pure O_2; 2- 48% O_2 mixture; 3- 70,5% O_2 mixture; 4- 83,3% O_2 mixture; 5-air.

$\tau_0 \cong k_1 \cdot [O_2] \cdot P \cong 10^{-3}$ s, where $k_1 = 7 \cdot 10^{-34}$ cm^6/s - the constant rate of reaction (1). So under our conditions $\tau_0 \ll 1/f$ is justly and velocity of ozone producion, observed in experiments with improved time resolution, is limited by velocity of oxygen atoms creation in discharge.

Ozone is mainly destructed in the reaction

$$NO + O_3 \rightarrow NO_2 + O_2, \qquad (2)$$
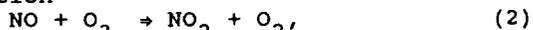
where NO molecules are produced in the reaction of nitrogen atoms with molecules of oxygen:

$$N + O_2 \rightarrow NO + O \qquad (3)$$

There are also reactions of ozone destruction by oxygen atoms:

$$O + O_3 \rightarrow Prod \qquad (4)$$

Reaction of O_3 destruction by metastable oxygen $O(^1D)$ is not importante in our conditions due to the rapid quenching of oxygen metastable atoms.

Estimation and computer modeling show that production of ozone in our system may be explained by molecular oxygen dissociation in discharge and than O-atoms conversion into ozone. Ozome destruction may be explained by slow accumulation of nitric oxides and its reactions with ozone.

Estimations also show that vibrational excitation of molecules and hydrogen impurities may influence on the ozone production. At low pressures (P≤20 Torr) diffusion of the O-atoms to the walls of discharge chamber may be significant.

5. CONCLUSION

Represented experimental results indicate that at the gas pressure in ozone layer 10-30 Torr the discharge in the form of breakdown ionization wave generate efficiently ozone at near natural concentrations.

The efficiency of ozone production permits to enrich ozone layer using this ozone generator situated at high altitude balloons. The estimation show that the utilizing of the set-up, based on the discharge, with an output of 1 kW, allows to product $5 \cdot 10^{12}$ cm^{-3} ozone concentration in V=35 m^3 volume for one second.

This type of discharge may also be used for the purposes of ozone kinetics laboratory investigation and modeling of ozone layer destroying.

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