

# STUDY OF OZONE DESTRUCTION REACTION ON SURFACES

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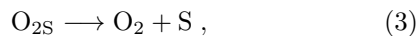
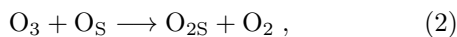
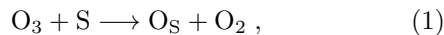
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**Abstract.** The ozone destruction was studied in a quartz cuvette. The time dependence of ozone concentration was measured by absorption spectroscopy. From this time dependence the pseudo first-order rate constant was derived. This rate constant depends on surface condition - the surface concentration of adsorbed oxygen atoms. This surface concentration was changed by reactions of adsorbed oxygen atoms with gaseous molecular oxygen just before the cuvette was filled by ozone. The decrease of atomic oxygen surface concentration leads to the decrease of rate constant for ozone destruction. The measured rate constants were in range  $9.0 \times 10^{-5} \text{ s}^{-1}$  to  $9.8 \times 10^{-5} \text{ s}^{-1}$ .

**Keywords:** ozone, destruction, surface reaction.

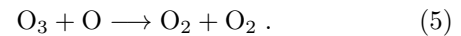
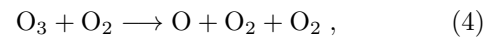
## 1. Introduction

Ozone is a strong oxidizing agent with significant applications across various fields such as wastewater treatment [1], air pollution control [2], chemical etching [3], biomedical application [4], agriculture [5], and more. Its primary production occurs within dielectric barrier discharges (DBDs), especially those burning at atmospheric pressure [6]. Extensive research, both experimental and theoretical, has been conducted to understand ozone generation within these discharges, typically focusing on volume reactions [7]. However, recent observations by Taguchi et al. [8] revealed a gradual decrease in ozone concentration within DBDs burning in pure oxygen (99.99995%). The exact mechanisms of this effect, which destroys the ozone, are still not understood. However, it was proposed that this decrease is due to surface reactions of ozone. The aim of this paper is to study the surface reactions leading to ozone destruction. The ozone can be decomposed as follows



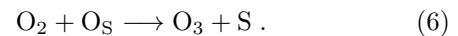
where S is the vacant chemisorption site at the surface,  $\text{O}_\text{S}$  and  $\text{O}_{2\text{S}}$  are atomic and molecular oxygen adsorbed on the surface. Ozone destruction on surfaces can also be influenced by factors such as surface morphology, temperature, humidity, and the presence of other reactive species. For example, the presence of water molecules on a surface can enhance ozone degradation through processes such as hydrolysis or formation of reactive oxygen species. On the other hand, the atomic nitrogen can be bind on the surface and thus it can block the ozone destruction.

The ozone can be also destroyed by following volume reactions in gas phase



The rate coefficients for reactions (4) and (5) are  $7.28 \times 10^{-14} \exp(-9300/T)$ , and  $9.52 \times 10^{-12} \exp(-2080/T)$ , respectively [9]. The reactions (4) and (5) are important at higher gas temperatures.

The ozone can be also created by surface reaction, the Eley-Rideal process of a gaseous oxygen molecule with adsorbed atomic oxygen leads to formation of gaseous ozone molecule



In our recent study [6], the ozone creation and destruction on electrode surface previously treated in oxygen DBD at atmospheric pressure were studied. In this paper, we show that the treatment of surfaces by ozone only (without any discharge) is sufficient to observe subsequent destruction of ozone by surface reactions.

## 2. Experiment

Experimental setup used for this study is shown in Fig. 1. Extremely high-grade oxygen of 99.9999% purity was led through the molecular sieve and the mass flow controller into the cylindrical ozonizer, which was used for ozone generation. The oxygen pressure was atmospheric and the flow was set to 2 slm. Ozonizer outer electrode was made of stainless steel (SS316L) and it was maintained at earth potential. The inner diameter of the outer electrode was 24 mm. The outer electrode was covered by alumina dielectric, which was 2.85 mm thick. The inner cylinder was a high voltage electrode and it was made of stainless steel (SS316L).

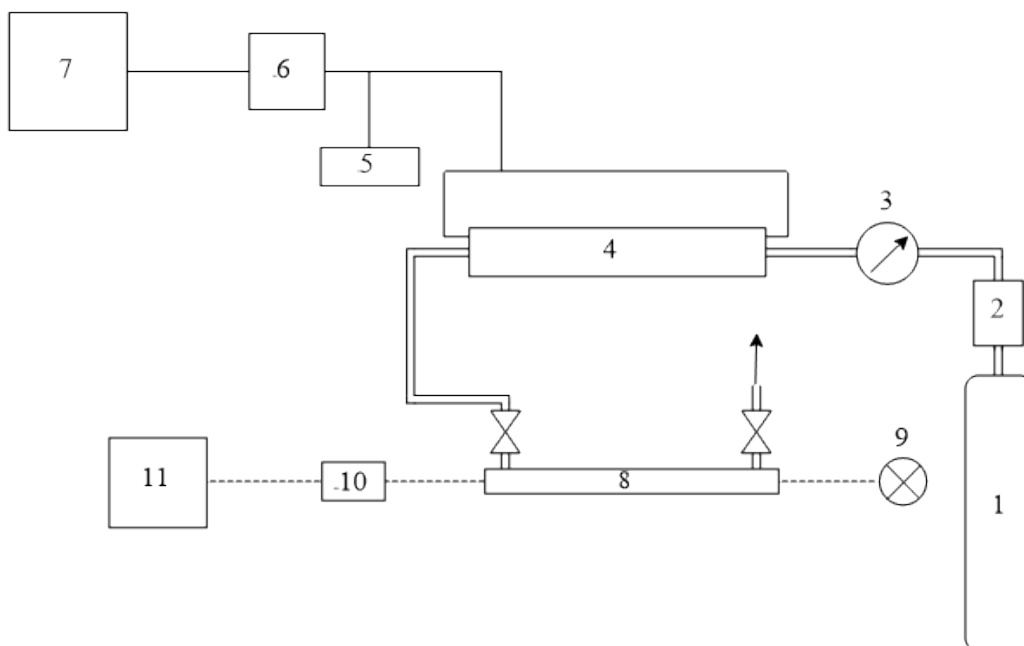


Figure 1. Experimental setup: 1 - gas cylinders with oxygen; 2 - zeolite molecular sieve; 3 - mass flow controllers; 4 - ozonizer; 5 - oscilloscope; 6 - transformer; 7 - high voltage power supply; 8 - quartz cuvette; 9 - deuterium lamp; 10 - spectrometer; 11 - computer

The outer diameter of the inner electrode was 17 mm, so the discharge gap was 0.65 mm thick. The length of the ozonizer was 240 mm. The cooling water flowed through outer electrode, the water temperature was controlled to be constant during the experiments. So the gas temperature did not exceed 300 K. The high voltage power supply operating at frequency 20 kHz and voltage amplitude of 4.5 kV was used to generate DBD in the ozonizer. The ozone was led through the quartz absorption cell (quartz cuvette). The cuvette length was 180 mm and the diameter was 12 mm. The cuvette was located between deuterium halogen lamp (Ocean Optics DT-Mini-2-GS) and grating spectrometer (Ocean Optics Red Tide USB 650UV). The light was transmitted into and from the cuvette by the optical fibres. The OAS spectra were measured in the range 200–850 nm. The ozone concentration was determined by absorption spectroscopy with time step of 0.1 s. The experiment with ozone surface destruction was performed as follows:

1. the cuvette was treated by flowing ozone for 30 min, the gas flow was 2 slm and the ozone concentration was  $4.8 \times 10^{18} \text{ cm}^{-3}$ ,
2. the ozonizer was switched off and the cuvette was blowing by pure oxygen for given time  $t_r$ ,
3. the ozonizer was switched on for 3 s and the cuvette was filled by ozone and closed,
4. the decrease of ozone concentration in the cuvette was measured.

The reaction time  $t_r$  was set to 0, 5 and 10 min.

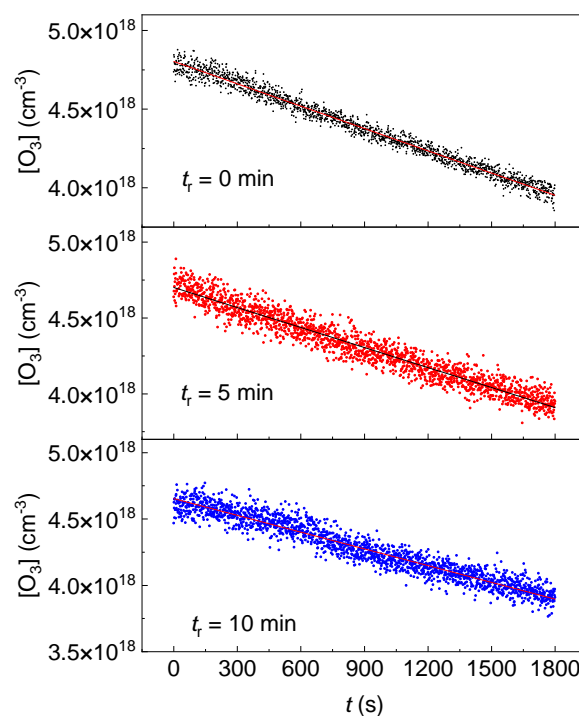


Figure 2. Time dependence of ozone concentration.

### 3. Results and Discussion

If the cuvette is treated by ozone, its surface is filled by adsorbed atomic oxygen via reaction (1). Then the cuvette is closed and the ozone in the cuvette is destroyed mainly by reaction (2). The reaction rate of this reaction is proportional to surface concentration of atomic oxygen. The surface concentration of atomic oxygen can be changed by reaction (6). So, if the

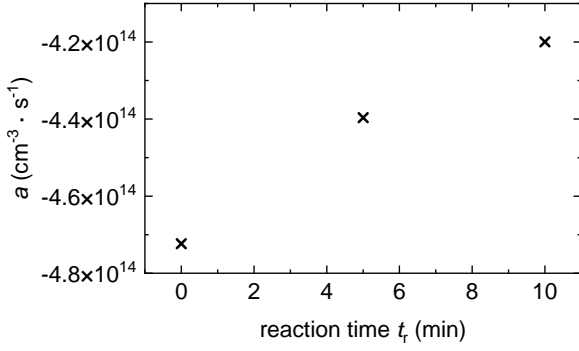


Figure 3. The values of the slopes.

cuvette surface is first treated by pure oxygen, the surface concentration of atomic oxygen decreases and subsequent rate of ozone destruction will be lower.

The time dependencies of ozone concentration for different reaction times  $t_r$  are shown in Fig. 2. The dependencies were fitted with a straight line and the slopes of these lines are shown in Fig. 3. As can be seen from Fig. 3 the absolute value of the slope decreases, so the reaction rate also decreases. Usually, the ozone destruction is described as pseudo first-order kinetic equation of the following configuration

$$-\frac{d[\text{O}_3]}{dt} = k[\text{O}_3], \quad (7)$$

where  $k$  is the pseudo first-order rate constant. The results from Fig. 3 provide values of  $k$  from  $9.0 \times 10^{-5} \text{ s}^{-1}$  to  $9.8 \times 10^{-5} \text{ s}^{-1}$ . These values represent the surface loss rates, because the gas reaction (4) and (5) can be neglected at the gas temperature used in our experiments (300 K). The minimum surface loss rate for quartz and temperature of 313 K was reported by Suzuki et al [9]. Their reported value was  $2.5 \times 10^{-5} \text{ s}^{-1}$ , which is four times lower than ours.

## 4. Conclusion

The ozone destruction in quartz cuvette was measured using the absorption spectroscopy for ozone concentration determination. The ozone concentration decreases linearly which allows to determinate the first order loss rate constant. It was shown that the ozone destruction is due to the surface reaction. The obtained rate constants depend on surface conditions, i.e. the surface concentration of oxygen atoms. The surface concentration of oxygen atoms can be changed by reactions of gaseous oxygen flowing through the cuvette. The rate constants were determined in the range from  $9.0 \times 10^{-5} \text{ s}^{-1}$  to  $9.8 \times 10^{-5} \text{ s}^{-1}$ .

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