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STUDY OF OZONE DESTRUCTION REACTION AT HIGHER TEMPERATURES

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Abstract. The ozone destruction at higher gas temperatures was studied in a quartz cuvette. The cuvette was heated by a resistance wire wound on the outer surface of the cuvette. The cuvette was filled with ozone and the time dependence of ozone concentration in the cuvette was measured by absorption spectroscopy. The rate constant for ozone decay was derived from this time dependence. The influence of the rate constant on surface condition (the surface concentration of adsorbed oxygen atoms and molecules) was studied. The surface concentration of adsorbed oxygen atoms was changed by reactions with gaseous molecular oxygen just before the cuvette was filled by ozone. The cuvette temperature was set to 40, 50 and 60 °C. The measured rate constants increase with increasing temperature from the value $1.27 \times 10^{-4}\ \mathrm{s}^{-1}$ to $1.88 \times 10^{-4}\ \mathrm{s}^{-1}$. The influence of temperature and cuvette surface coverage on ozone decay constants is discussed.

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 experimental and theoretical research 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%). This phenomenon is called Ozone Zero Phenomenon (OZP). The exact mechanisms of this OZP, 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

$$\mathrm{O_3} + \mathrm{S} \longrightarrow \mathrm{O_S} + \mathrm{O_2}\ , \qquad (1)$$

$$\mathrm{O_3} + \mathrm{O_S} \longrightarrow \mathrm{O_{2S}} + \mathrm{O_2}\ , \qquad (2)$$

$$\mathrm{O_{2S}} \longrightarrow \mathrm{O_2} + \mathrm{S}\ , \qquad (3)$$

where S is the vacant chemisorption site at the surface, $\mathrm{O_S}$ and $\mathrm{O_{2S}}$ are atomic and molecular oxygen species adsorbed on the surface. The species adsorbed on the surface can have different binding energies and therefore also different reactivities [9]. The reaction rates for reactions (1) and (2) are proportional to $\Phi \cdot \exp(-E_a/kT)$, where Φ is the ozone flux to the surface $\Phi = n_{\mathrm{O_3}}/4 \cdot \sqrt{8kT/\pi m_{\mathrm{O_3}}}$ and E_a is the activation energy corresponding to individual reaction.

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 the formation of reactive oxygen species.

The ozone destruction on the surface can be limited by adding a small amount of nitrogen to oxygen. Nitrogen is partially dissociated in the discharge and atomic nitrogen binds to an empty surface site. This site cannot then be occupied by atomic oxygen and cannot subsequently react with ozone. The bond of nitrogen atoms on the surface is probably stronger than the bond of oxygen atoms. Therefore, nitrogen binds preferentially to the surface and the bound nitrogen does not react with ozone. Therefore, a small amount of nitrogen is added when producing ozone from pure oxygen to suppress the OZP.

The desorption frequencies for adsorbed species are $\nu = \nu_0 \cdot \exp(-E_d/kT)$, where ν_0 is estimated to be $10^{13}\,\mathrm{s}^{-1}$ and E_d is desorption energy ($\sim 0.17 - 0.26\,\mathrm{eV}$ for $\mathrm{O_{2S}}$) [10].

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

$$\mathrm{O_3} + \mathrm{O_2} \longrightarrow \mathrm{O} + \mathrm{O_2} + \mathrm{O_2}\ , \qquad (4)$$

$$\mathrm{O_3} + \mathrm{O} \longrightarrow \mathrm{O_2} + \mathrm{O_2}\ . \qquad (5)$$

The rate coefficients for reactions (4) and (5) are $7.28 \times 10^{-14} \exp(-9300/T)\,\mathrm{cm^3\,s^{-1}}$, and $9.52 \times 10^{-12} \exp(-2080/T)\,\mathrm{cm^3\,s^{-1}}$, respectively [11]. The reactions (4) and (5) are important at higher gas temperatures.

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

$$O_2 + O_S \longrightarrow O_3 + S\,. \tag{6}$$

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

2. Experiment

The 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 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 an alumina dielectric, which was 2.85 mm thick. The inner cylinder was a high voltage electrode and it was made of stainless steel (SS316L). 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 the outer electrode, and the water temperature was controlled to be constant during the experiments. So, the gas temperature in the ozonizer did not exceed 300 K.

The high voltage power supply operating at a frequency of 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 inner diameter was 12 mm. The cuvette was located between a deuterium halogen lamp (Ocean Optics DT-Mini-2-GS) and a grating spectrometer (Ocean Optics Red Tide USB 650UV). The light was transmitted into and out of the cuvette by the optical fibres. The OAS spectra were measured in the range 200–850 nm. The cuvette was heated by a resistance wire wound on the outer surface of the cuvette. The cuvette temperature was measured by CEM DT-613 thermometer on cuvette outer surface. Preliminary experiments showed that the temperature of the cuvette inner surface is only 4 °C lower. The ozone concentration was determined by absorption spectroscopy with a time step of 0.1 s. Detailed information on ozone concentration determination can be found in our previous paper [12].

The experiment with ozone surface destruction was performed as follows:

1. the cuvette was heated to a given temperature,
2. the cuvette was treated by flowing ozone for 30 min,
3. the ozonizer was switched off and the cuvette was blown by pure oxygen for a given time t_r,
4. the ozonizer was switched on for 3 s and the cuvette was filled with ozone and closed,
5. the decrease of ozone concentration in the cuvette was measured.

The reaction time t_r was set to 1, 5 and 10 minutes.

3. Results and Discussion

When the cuvette is treated by ozone flowing through the cuvette, its inner surface is covered by adsorbed atomic and molecular oxygen via reactions (1) and (2). When the cuvette is closed with the ozone inside, the ozone in the cuvette is again destroyed by reactions (1) and (2) and its concentration decreases.

The reaction rate of reaction (2) is proportional to the surface concentration of atomic oxygen. The surface concentration of atomic oxygen can be changed by reaction (6). So, suppose the cuvette surface is first treated by pure molecular oxygen flowing through the cuvette. In that case, the surface concentration of atomic oxygen decreases and subsequent rate of ozone destruction via reaction (2) will be lower. The reaction rate of reaction (1) is proportional to the surface concentration of vacant chemisorption sites. However, these sites can be filled by molecular oxygen, so they cannot participate in reaction (1). If the temperature increases, the desorption rate and the destruction rate of ozone via reaction (1) also increases.

The time dependencies of ozone concentration for different ozone temperatures and reaction time $t_r = 1$ min are shown in Fig. 2. The gas pressure in the cuvette is atmospheric, so the initial ozone concentration decreases with increasing temperature. The ozone concentrations decrease linearly, so their dependencies were fitted with a straight line and from the slopes of these lines the rate constants were calculated. Usually, ozone destruction is described as a pseudo first-order kinetic equation of the following formula

$$\frac{\mathrm{d}n_{O_3}}{\mathrm{d}t} = -k n_{O_3}\,, \tag{7}$$

where k is the pseudo first-order rate constant. This rate constant includes the ozone losses caused by both reactions (1) and (2). The solution of this equation can be approximated for short times t as $n_{O_3} = n_0(1 - kt)$, where n_0 is the initial ozone concentration. The calculated rate constants are shown in Fig. 3. The calculated uncertainty of the rate constants was less than 1%. The values of the rate constant at room temperature were taken from our previous paper [13]. As can be seen from Fig. 3, the rate constant for ozone decay increases with increasing temperature except the rate constant at the temperature of 60 °C and reaction time of 10 min. The results from Fig. 3 provide values

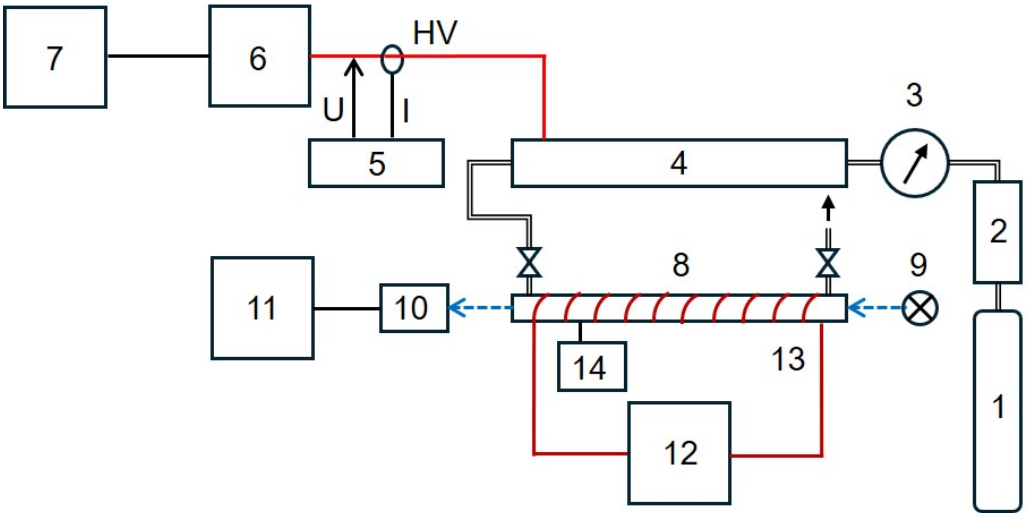

Figure 1. Experimental setup: 1 - gas cylinders with oxygen; 2 - zeolite molecular sieve; 3 - mass flow controllers; 4 - ozonizer; 5 - oscilloscope; 6 - transformer; 7 - high voltage power supply; 8 - quartz cuvette; 9 - deuterium lamp; 10 - spectrometer; 11 - computer; 12 - power supply for heating; 13 - heating resistance wire; 14 - thermometer.

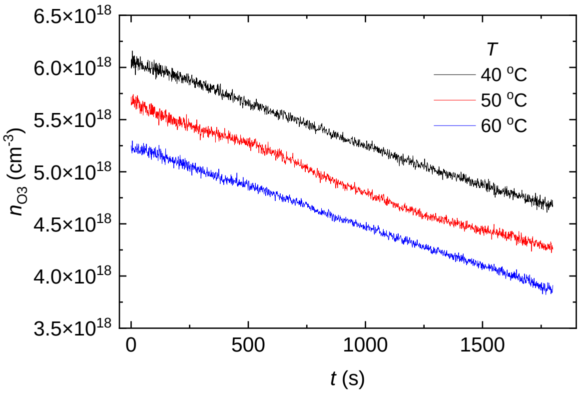

Figure 2. Time dependence of ozone concentration for different ozone temperatures T and reaction time $t_\mathrm{r} = 1$ min.

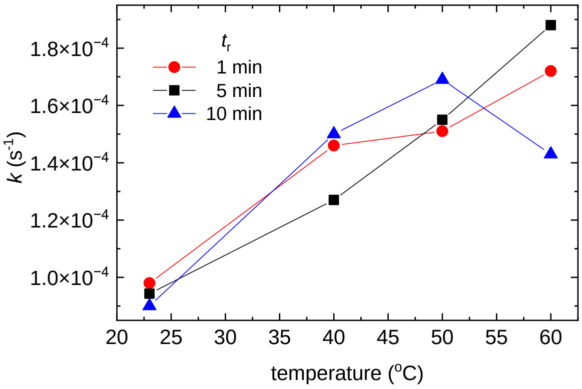

Figure 3. The values of the rate constants for different ozone temperatures T and reaction times t_r.

of k from 1.27×10^{-4} s^{-1} to 1.88×10^{-4} 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 (up to 60 °C). The influence of temperature on individual reactions is as follows: The ozone flux Φ to the surface decreases with temperature at constant (atmospheric) pressure as $1/\sqrt{T}$. The rate constants for reactions (1) and (2) depend on factor $\exp(-E_a/kT)$, which is a strong temperature dependence. The same is valid for the desorption rate. The increase of the rate constant for ozone destruction is due to these exponential dependencies. The dependence of the rate constant on the reaction time t_r of oxygen surface treatment was not proven with measured data. The experiments are influenced by the initial surface state, which is difficult to prepare in the same state in all experiments. To exclude the influence of the surface condition on individual measurements, the measurements under different conditions were performed in a series one after the other. The exception was the measurement at 60 °C and reaction time of 10 min, which was performed one day after the previous measurements. This fact could explain the decrease of rate constant measured under these conditions.

The minimum surface loss rates of ozone for quartz and temperatures of 40 °C and 60 °C were also determined by Suzuki et al [11]. Their reported values for temperatures of 40 °C and 60 °C were 2.5×10^{-5} s^{-1} and 4.6×10^{-5} s^{-1}, respectively. However, Suzuki et al used the cuvette with an inner diameter of 24 mm. The influence of surface processes on volume ozone concentration in simple kinetic models is included with a factor S/V, where S is the inner surface area and V is the inner volume of the reaction chamber (in this case, the cuvette) [10]. The factor S/V for a long cylindrical chamber equals $2/R$, where R is the inner radius of the reaction chamber. So, the Suzuki et al rate constants must be at least two times lower than ours, because their cuvette had a two times larger radius.

4. Conclusion

The ozone destruction in the quartz cuvette was measured using absorption spectroscopy for ozone concentration determination. The ozone concentration decreases linearly, which allows us to determine the first order loss rate constant. It was shown that the ozone destruction is due to the surface reaction. The obtained rate constants increase with increasing temperature. The initial surface concentration of oxygen atoms can be changed by reactions of gaseous oxygen flowing through the cuvette, however, the presented experiments did not prove the influence of initial oxygen atom surface concentration on ozone decay. The rate constants were determined in the range from 1.27×10^{-4} s^{-1} for temperature of 40 °C to 1.88×10^{-4} s^{-1} for temperature of 60 °C.

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