Kinetics of ozone production by surface processes

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Plasma surface interactions are of considerable importance for a wealth of discharge phenomena. They are especially important in the formation and destruction of ozone in the afterglow of a DC low-pressure discharge in pure O_2 [1] and also in a dielectric barrier discharge at atmospheric pressure [2]. Nevertheless, the rates or probabilities associated with these surface reactions remain unknow. This contribution focuses on elucidating the determination of ozone production rates on silica surfaces.

When the solid surface is into contact with oxygen discharge or ozone, the surface is quickly covered by adsorbed atomic oxygen species and also by molecular oxygen species. Then the ozone is created by surface reactions via Langmuir-Hinshelwood (LH) mechanism or via Eley-Rideal (ER) mechanism. The LH mechanism is described by reaction

$$O_{2S} + O_S \rightarrow O_3 + 2S, \quad (1)$$

where O_S and O_{2S} are adsorbed oxygen atoms and molecules, respectively, S is the vacant site. The ER mechanism is described by reaction

$$O_2 + O_S \rightarrow O_3 + S, \quad (2)$$

where O_2 is molecule arriving at the surface from gas phase. These reactions were studied in the experimental set-up shown in Fig.1.

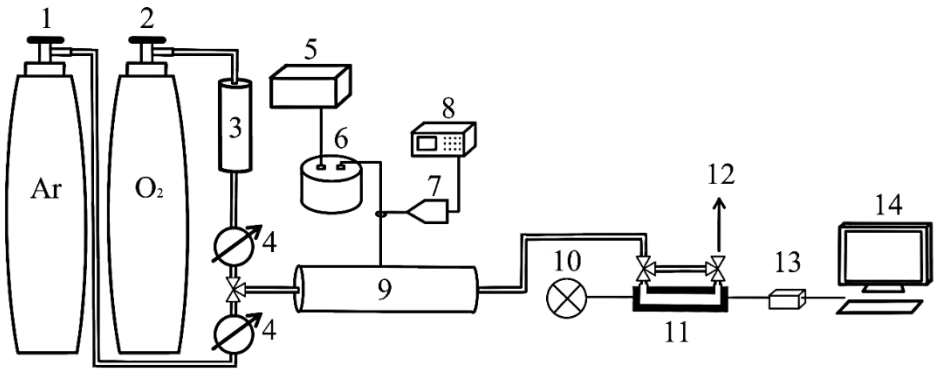

Fig.1: 1 – argon bottle, 2 – oxygen bottle, 3 – zeolites, 4 – mass flow controllers, 5 – high voltage generator, 6 – transformer, 7 – high voltage probe, 8 – oscilloscope, 9 – ozonizer, 10 – light source, 11 – measuring cuvette, 12 – gas outlet, 13 – spectrometer, 14 – PC.

The inner surface of the cuvette was treated by ozone for 5 min. After that the ozone was removed from the cuvette and the cuvette was filled by the mixture of oxygen and argon with different ratio. The time dependence of originated by surface reaction was measured using absorption spectroscopy. The results are shown in Fig.2. For short reaction time the ozone concentration increases linearly, when the ozone concentration increases above $2 \cdot 10^{14}$ cm^{-3} also the destruction processes of ozone occur. When the cuvette is filled by argon only, the ozone originated by LH processes only. If the oxygen is added to the argon, the ozone is created also by ER mechanism and the increase of ozone concentration is faster and

the final ozone concentration is also higher, see Fig.2. The ozone concentration produced by LH mechanism is described by equation

$$n(O_3) = \frac{2}{R} \cdot \frac{n_0^2(O_S) \cdot k \cdot t}{1 + n_0(O_S) \cdot k \cdot t} \quad , \tag{3}$$

where R is the cuvette radius, $n_0(O_S)$ is the initial surface concentration of adsorbed O atoms, k is the rate coefficient and t is the time. For short times this equation (3) reduces to

$$n(O_3) = \frac{2}{R} \cdot n_0^2(O_S) \cdot k \cdot t \, . \tag{4}$$

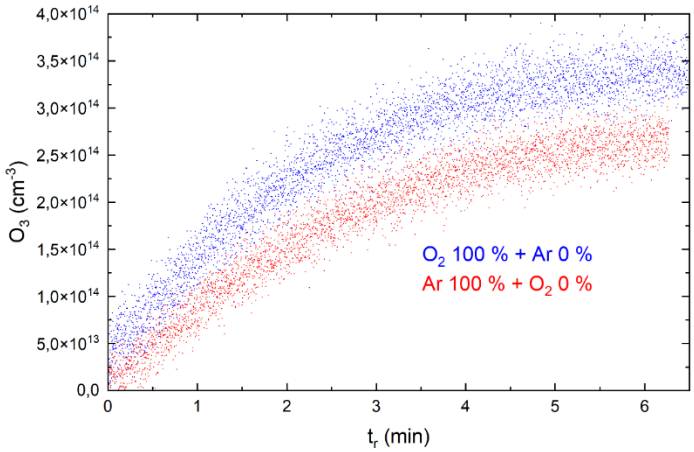

Fig.2: The dependence of ozone concentration on reaction time.

So, the initial slope of time dependence of ozone concentration is $a = \frac{2}{R} \cdot n_0^2(O_S) \cdot k$. The slopes are shown in Fig. 3.

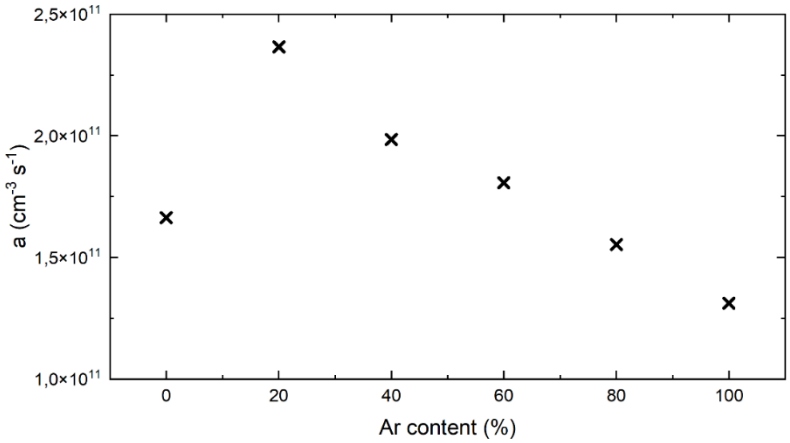

Fig.3: The dependence of the initial slope on argon content in the mixture.

We assumed that the surface concentration of active sites is 10^{16} cm^{-2} and one half of these sites is occupied by atomic oxygen and second half is occupied by molecule oxygen. Under this assumption the rate coefficient derived from these slopes is $1.56 \cdot 10^{-20}$ cm^{-2}s^{-1} for LH mechanism and for ER mechanism is $1.0 \cdot 10^{-28}$ cm^{-2}s^{-1}.

[1] J. P. Booth et al, *Plasma Sources Sci. Technol.* **32** (2023) 095016.
[2] M. Meyer, J. Foster and M. J. Kushner. *Plasma Sources Sci. Technol.* **32** (2023) 085001.

Acknowledgement

This research work was supported by the Project for the Development of the Organization "DZRO Military autonomous and robotic systems" under Ministry of Defence and Armed Forces of Czech Republic.