Macrokinetics of the ozone synthesis process in silent discharge conditions

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Abstract

The method of the determination of elementary processes, constant for silv discharge, presented in the modified KJH report that inspired method of determining of the specific charges was applied. A novel method of determining of initial threshold ozone concentrations with experimental data was obtained.

1. Introduction

The non-thermal plasma reactors that converters belong to devices in which the determination of gas temperature is very problematic. It results from the occurrence of elementary processes proceeding in these reactors with the participation of electrons initiating sequential reactions that participate of atomic oxygen or nitrogen in very short time in a not too large volume of the discharge gap. After the disappearance of discharge the chemical reactions can not only in the space occupied formerly by micro-discharge channels but in all space between electrodes [1]. This causes the occurrence of local concentration gradients or reacting particles and temperature gradients. Therefore chemical processes proceed in diversified thermal conditions although generally the reactants of the reaction systems prior to the compensation of these differences.

Sample and quite effective manner to affect the gas temperature inside the discharge gap could be the thermostating of the electrodes. Unfortunately, even if the gap between the electrodes is small cooling media affect mostly the temperature of the electrodes' surface and the gas temperature (mass-averaged between them) is still difficult to predict. This is so since under silent discharge conditions the heat exchange between the gas and cooling liquid takes place through the turbulent layers, and hence it is considerably more difficult. Since the gas temperature influences the rate of the proceeding chemical reactions, it is the most important parameter in determining the kinetics of the ozone synthesis process.

2. Apparatus and Measurement Procedure

A glass ozonizer with the active length of the electrodes of 10 cm and the width of the discharge gap of 3.5 mm was used. A double-walled vessel of thermostating the discharge gap was applied. The ozonizer was supplied with AC at frequency of 3 kHz and voltage amplitude of up to 11 kV. The measured active power of discharge was up to 95 W. A density of energy input up to 13 kW/m². Experiments were carried out at 0, 25 and 50°C of the fluid cooling the
electrode walls. A closed circuit of the non-conducting cooling liquid was applied to the reactor to remove the heat generated in the reaction. The temperature of the solution did not exceed 40°C. The ozonator was filled with oxygen with water vapor content of 1.4 ppm. The flows of oxygen were 4.5 L, 2.5 L, and 1.0 L/min. The ozone concentration in 4 ppm solution was measured by an OMM 506 device. Discharge active power was measured by a noise disturbance meter SM 1000 by Alline Polanit. Measurements for particular discharge powers were performed until achieving complete stabilization of the ozonator's operating conditions, which usually took several tens of minutes.

3 Results

The results obtained for all flow rates, ozone concentrations, and temperatures at 5°C and 40°C were the basis for calculating the rate constants of ozone formation k and decomposition k. The Van't Hoff equation modified to the following form was used [1, 3]:

\[
\ln \left( \frac{a}{a_0} \right) = \frac{-E_a R T}{n F} \left( \frac{1}{T} - \frac{1}{T_0} \right)
\]

with the notation for respectively a and T, whereas the k, E_a, k, and T_0 were determined. The constant k has been determined from analysis of the following equation:

\[
\ln \left( \frac{a}{a_0} \right) = \frac{-E_a R T}{n F} \left( \frac{1}{T} - \frac{1}{T_0} \right)
\]

where:

- a - experimental data of the ozone content, mole fraction
- a_0 - threshold ozone content, mole fraction
- E_a - activation energy, kJ/mol
- k - constant rate of ozone decomposition, kJ/mol
- n - total mole concentration, mol/mol

However, the data for calculations did not originate directly from the experiment, but were corrected in such a way as to successively eliminate the effects of temperature changes in the course of chemical reactions. The procedure applied will be explained in detail in part of the paper.

Figure 4 presents an example of the results obtained at 40°C in the form of experimental points and interpolation curves to express the relationship between ozone concentration a and active power P_a applied to the ozonator for the respective values of \( V \). Analogous results were obtained for the other temperatures. Of course, the ozone concentration obtained at 40°C was for all flow intensities, respectively, higher than at 5°C and at 0°C, consequently lower than shown in the figures. The results were used as a basis for composing data of ozone concentration values at as a function of constant values of both V and P_a. Such a conversion enables the interpretation of the kinetic-thermocharacteristics of the process and enables its representation in terms of a relationship between ozone concentration on one hand and active power and residence time of reactants in the discharge zone on the other \( n = f(P_a, V) \). In the term \( V \) corresponds to the residence time of one of the characteristics obtained exhibits a monotonic increase of ozone concentration with increasing residence time, \( V \), and flattening of the surface observed at higher \( V \) values suggests that the ozone concentration approaches to an limiting value. Somewhat different is the relationship between ozone concentration and active power \( P_a \). A monotonic increase of ozone concentration \( a \) with increasing \( P_a \) is observed only in the region of \( V \), small values, whereas for large values of \( V \), the concentration of ozone after
having reached a maximum, decreases with increasing $P_A$

The data presented in Fig. 1 have been transformed to a relationship $a = a(P_A)$ for constant values of active power $P_A$. In terms of equation $P_A = \alpha(T)$,

This analysis has resulted in a relationship $a = a(T)$ for the parameter $\alpha$. The values of constants $a$, $k$, $n$, and $P_A$, as well as the value of parameter $k$, have been determined. Such a procedure may be justified as follows. The V.K.L. formula comprises temperature-dependent parameters $a$, and $k$. Since temperature at the point of measurement is always dependent on the stream of energy supplied, the analysis gives the values of $n$ and $P_A$, related to a constant value of $P_A$, to equation (6) should give better conformity of the V.K.L. formula with experiment than is obtained in a case where different $P_A$ values are concerned. This effect is visible in Fig. 2, where the $P_A$ and a decrease of the ozone concentration occurs.

![Diagram 1: Ozone concentration vs active power at temperature 38.4°C](image1)

![Diagram 2: Ozone concentration vs both active power and inverse of gas density, 21.4](image2)

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Fig. 3 shows calculated values of limit ozone concentration as a function of active power. All curves after a period of increase in the region of small powers attain a maximum and then slowly fall down. The mutual position of the curves is in full agreement with the results of experiments. The lower the temperature, the higher the ozone concentration. In Fig. 4 are presented the calculated values of constants $k$ and $k$. As can be seen, the rate constants of ozone formation accept values practically independent of power and temperature, whereas decomposition rate constants show a clear relationship on temperature. Within a range of temperature the $k$ values noticeably increase. In the range of small powers below 500 W the $k$ constants decrease until reaching practically constant values.

![Diagram](image)

Fig. 3: Calculated threshold ozone concentration after following absorbed active power $P_w$.

![Diagram](image)

Fig. 4: Calculated ozone formation $k$, dashed lines and decomposition reaction rate constants $k$, solid lines.
4 Discussion

The results presented in Figures 3 and 4 result from the calculation of parameters in the VSI equation, which was derived with some simplifying assumptions. It is assumed, among others, that specific energy is an independent parameter. In reality it is composed of two basic parameters of the process: the voltage and gas temperature. Each of them is dependent on other processes, such as the voltage at certain, achieved as well as the gas temperature in the discharge gap. The same holds true for small powers and small gas flow rates as well as for large powers and large flow rates. However, due to the power increase accompanied by intensive heat exchange in the gap, which is only to a small extent withdrawn by the flowing gas, it is still possible to measure the temperature in the gap itself. As an effect, the atomic concentrations assigned to the discharge gases in the gap increase by a factor of several thousand times. Such an occurrence often causes a decrease in the reaction rate and other parameters, which cannot be achieved without changing the experimental conditions. In this case, the discharge gap width, diameter of the electrode material, electrical characteristics, and other factors influence the phenomenon.

In order to have a better idea of the temperature in the enzyme's gap due to an increase in the supply voltage, the simulations were performed against data corrected from experimental results. Results of the experiments on the error resulting from such a correction procedure are not large, which can be observed when analyzing Figures 3 and 4 in the W region. However, in the range of small powers the accuracy of this method is not as large. The results have several reasons. First of all, the accuracy of small power measurements is not as good as for large powers. This causes the possibility of introducing relatively large measurement errors in this region, which during the interpolation of the experimental results may cause essential deviations of sinusoidal data. Moreover, in the small power range, in other words, exceeding the necessary voltage, the discharge gap may not be filled from the solution covering the electrode space.

In the range of powers above 10 W at which the effects resulting from the interpolation are negligible, both the data calculated as well as ozone decomposition rate constant values at particular temperatures can be assumed as constant. It is worth noting that the calculated limiting ozone concentrations are in good agreement with the experimental data obtained for very small flow intensities of 5 cm³/min, which should be close to threshold concentrations. The small differences result from the fact that the experimental data are burdened to a greater degree with the influence of temperature than data used in calculations, since the measurements were carried out at increasing power and nearly still gas in the gap.

From the calculations presented above, one can see that the ozone synthesis mechanism at the gas temperature in the discharge gap quite considerably affects the ozone decomposition, but it practically does not influence the rate of its synthesis. This is in agreement with the generally acknowledged process mechanism, in which only oxygen radicals (O·) and O participate in the ozone formation. The rate of these reactions does not depend on temperature at 1 MPa.

\[
\begin{align*}
\text{O}_2 & \rightarrow \text{O} + \text{O} \quad (a) \\
\text{O} + \text{O}_2 & \rightarrow \text{O}_3 \quad (b) \\
\text{O}_2 + \text{O} + \text{M} & \rightarrow \text{O}_3 + \text{M} \quad (c)
\end{align*}
\]
\[ \text{O} + \text{O} \rightarrow \text{O}_2 \quad (4) \]
\[ \text{O} + \text{M} \rightarrow \text{O} \cdot \text{M} \quad (5) \]

The rate of the photochemical reactions clearly depends on temperature which affects the ozone concentration decrease.

![Graph showing the relationship between \(P_{\text{W}}\) and \(a\text{O}_3\text{ mole}\%\).]

**Fig. 5**: Measured ozone threshold ozone concentration. \(a\text{O}_3\text{ mole}\%\) as a function of \(P_{\text{W}}\). \(\triangle\), \(\bullet\), \(\square\): flow rate \(8\) \(\text{Nmlh}\). \(\bigtriangleup\), \(\bigbullet\), \(\bigsquare\): flow rate \(16\) \(\text{Nmlh}\).

5. **Conclusions**

The VSI equation in the modified version enables to characterize the mass transfer of the ozone synthesis process. The assumed method of converting experimental data neutralizing the effect of temperature connected with current flow through the discharge permits to a more accurate estimation of the phenomena occurring in the discharge zone than in direct analysis of the experimental data. The necessity of maintaining constant conditions in the interpolation of data, especially in the range of small discharge powers, is a considerable limitation of this method.

**References**