OZONE FORMATION IN DIELECTRIC BARRIER DISCHARGES
IN OXYGEN

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ABSTRACT

A theoretical description of ozone formation in a silent discharge is presented. Electron-impact dissociation in the microdischarge channels is calculated with the aid of the Boltzmann equation. Formation of O₃ from O is determined by considering many excited states in addition to the well known ground state reactions. Predictions of maximum efficiency and O₃ concentrations show remarkable agreement with experiments.

I. INTRODUCTION

Ozone is increasingly used for the treatment of drinking water as well as a bleaching and oxidizing agent that causes no environmental problems. Ozone synthesis in gas discharges has become one of the most important plasma chemical processes. Several of the larger installations used for the purification of drinking water reach the megawatt level. New plants under construction now for the elimination of NOₓ from the flue gas of power plants will produce tons of ozone per hour at power levels of tens of megawatts.

Our theory of ozone generation in a silent discharge takes the physical as well as the chemical aspects into account. In this paper we expand our theory to include vibrationally excited O₂. The measured quantities are influenced by discharge processes, e.g. dissociation of O₂ by electron impact, as well as by chemical reactions involved in the formation of O₃ from oxygen atoms. The matter is further complicated by the presence of excited and charged species and the fact that the silent discharge is extremely inhomogeneous with respect to space and time. The presence of the dielectric with its current limiting properties leads to a large number of discrete microdischarges of nanosecond duration. A realistic theoretical treatment of ozone formation in such discharges has to take the local transient conditions in these microdischarges into account. In the following we are going to describe a model that successfully predicts the efficiency of ozone generation and explains the major experimental trends.

II. PHYSICS OF OZONE FORMATION
THE DISSOCIATION PROCESS AND MAXIMUM EFFICIENCY.

Using published electron impact cross sections for oxygen we solve the Boltzmann equation for the electrons. With the distribution function of the electron energies we calculate the various excitation rates
to the corresponding levels of the $O_2$ molecule and the energy branching ratios (Fig.1). It turns out, that in the reduced field range 100 Td < E/N < 300 Td roughly 80% of the electron energy can be utilized for the dissociation of $O_2$:

$$e + O_2 \rightarrow e + O_2^* \rightarrow e + 20$$

(1)

Dissociation proceeds via two excited levels at 6 and 8.4 eV respectively (4).

It can be shown that each oxygen atom does form an $O_3$ molecule according to the reaction

$$O + O_2 + M \rightarrow O_3 + M$$

(2)

as long as the relative atom concentration $x_{10} = [O]/[O_2] < 10^{-4}$ and no ozone background is present.

Since ionic processes contribute only negligibly to ozone formation it is essential to ensure that most of the energy is fed into the electrons. Our calculations show that energy losses to ions can be drastically reduced if the current pulse in a microdischarge is sufficiently short (< 10 ns) and if the residual field and/or the ion density decays fast enough. Under these restrictions the maximum attainable efficiency calculated from some 70 rate equations involving reactions among the species $O^-(P)$, $O^+(D)$, $O_2^+$, $O_2(a^3 \Pi_g)$, $O_3(b^3 \Sigma_g^+)$, $O_3^+$, $O^+$, $O_2^+$, $O^+$, $O_2^+$ is given in Fig.2. The efficiency, based on direct electron impact dissociation only is given by the simple relation

$$\eta = 2 \frac{\rho_{\text{diss}}}{v_d \ E/N}$$

(03 molecules/eV)

(3)

where $\rho_{\text{diss}}$ is the dissociation rate coefficient and $v_d$ the electron drift velocity. The results obtained with Eq. (3) deviate only by few percent from the exact numerical values. This indicates that dissociation of $O_3$ molecules and subsequent formation of $O_3$ from oxygen atoms is, in fact, the main path to ozone formation.

The best experimental efficiencies reported are .13 $O_3$ molecules/eV for a normal silent discharge and .17 $O_3$ eV for special pulsed discharges (4). This corresponds to 60-80% of our theoretical maximum value of 0.22 $O_3$ eV. This indicates that the optimized silent discharge approaches the stated ideal conditions.

III. CHEMISTRY OF OZONE FORMATION

A. SINGLE PULSE IN PURE OXYGEN.

Even if ion losses can be neglected we don't quite reach the predicted optimum efficiency in a silent discharge. The reason is the incomplete conversion of oxygen atoms to $O_3$ due to other chemical processes.

There are mainly two reactions that reduce the efficiency of ozone formation if the concentration of oxygen atoms reaches a certain level: The recombination resulting in $O_2$ formation

$$O + O + M \rightarrow O_2 + M$$

(4)
and an enhanced ozone destruction due to excited ozone molecules

\[ O_3^* + O \rightarrow O_3 + O \quad (70\%) \] (5a)

\[ \rightarrow 2O_2 \quad (30\%) \] (5b)

Most ozone molecules formed by reaction (2) will initially be in an excited state (5). Many of these excited \( O_3 \) molecules will be quenched by \( O_2 \) or \( O \), but some will react according to reaction (5b) (Ref.6, Fig.3).

From different experiments like the temperature variation of the efficiency and admixtures of \( NO_2 \) we conclude that the relative atom concentration in the microdischarge channels in a typical silent discharge configuration is of the order of \( 10^{-3} \) (for a 1 mm gap at 1 bar) and increases with increasing pressure(7). It is thus by orders of magnitude larger than was previously assumed(8,9). The first direct measurement of high local oxygen atom concentrations in a dielectric barrier discharge has recently been obtained by W. Viööl(10). For the calculation of the reactions following a current pulse we have to take into consideration the conditions in the regions where we have oxygen atoms, that is in the narrow channels left behind by the microdischarges. After the recombination of electrons and ions, i.e. within nanoseconds of the electron pulse, most quantities like pressure, temperature etc. are close to average values. Only the atom concentration, the newly formed ozone and possibly some excited species will locally and transiently surpass average values. As Fig.3 shows, an atom concentration of \( 10^{-3} \) will reduce the efficiency of a single pulse close to measured values.

B. CONCENTRATION BUILD UP

A volume element travelling through an ozonizer discharge is subjected to the influence of a large number of microdischarges which gradually build up the ozone concentration. Calculations show essentially three regions (Fig.4):

I) Linear range, small influence of background ozone,
II) curved part, increasing influence of background ozone,
III) level part, ozone formation saturates, each additional pulse destroys as much ozone as it creates.

To explain the measured saturation limits one has to consider a number of processes in addition to the well known ozone destruction reaction

\[ O + O_3 \rightarrow 2O_2 \] (6)

These involve excited states

\[ A^* + O_3 \rightarrow \text{products} \quad (A = O, O_2, O_3) \] (7)

as well as electronic collisions

\[ e + O_3 \rightarrow e + O_2 + O \] (8)
Many of the reactions involving $\text{O}_2^+$ are not well documented. The same is true for Reaction 8. We get best agreement with our measurements if we assume that the ratio of the dissociation rates of $\text{O}_3$ and $\text{O}_2$ is about 5.

IV. COMPARISON WITH MEASUREMENTS

The quantities measured in ozonizer research are the integral efficiency and exit ozone concentration of a volume element entering the discharge with zero ozone concentration and reaching an exit concentration depending on the specific energy or number of microdischarges the volume element was subjected to. The plot efficiency vs. concentration has a very characteristic form (Fig.5) and is used for a comparison of our calculations and measurements. The measurements were made with an annular discharge gap of 1 mm width and 1 m length. The outer electrode was a water-cooled steel cylinder, the inner electrode a pyrex tube of 1.8 mm thickness. The saturation concentration depends strongly on temperature and pressure. In Fig.6 we test our model over a wide temperature and pressure range to predict the saturation concentration. The relative oxygen atom concentration was assumed to increase quadratically with gas density. The agreement between prediction and measurement is remarkable.

Our measurements were restricted to pressures at and above 1 bar. The rise of the saturation concentration at lower pressures has been investigated by several authors(11-13). It should be pointed out that the height and position of the maximum are influenced by the gap spacing. The general shape of the curve, however, will remain similar.

The comparisons of calculations and measurements show that our proposed model can predict the two main features of ozone generation namely the maximum efficiency and the saturation concentration over a wide parameter range.

REFERENCES

(10) Viöll, W., Diplomarbeit, University of Düsseldorf 1985.
Fig. 1: Distribution of electron energy losses due to different excitation processes in molecular oxygen (1 Td = $10^{-17}$ Vcm$^2$).

Fig. 2: Maximum attainable efficiency of ozone generation.

Fig. 3: Single pulse ozone generating efficiency vs. initial concentration of oxygen atoms $x_0 = [O]/[O_2]$. 

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Fig. 4: Build up of ozone concentration vs. specific energy (p=1 bar, T=278 K).

Fig. 5: Normalized efficiency vs. concentration curve (p=1 bar, T=278 K).

Fig. 6: Ozone saturation concentration vs. pressure ($x_{3s} = [O_3]/N$, E/N = 120 Td).