OPTIMIZATION OF OZONE PRODUCTION IN A PULSED HOMOGENEOUS OXYGEN DISCHARGE

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ABSTRACT

A theoretical model is presented which describes the kinetics of ozone formation in an atmospheric pressure transient glow discharge. Results are given on the different time scales involved. The calculations predict increased efficiencies for sub-microsecond pulses.

1. INTRODUCTION

It is well known that in many different types of electrical discharges in air or oxygen small amounts of ozone are generated. However, the efficiency of ozone production in a discharge is, in most cases, rather poor. The most important type of industrial ozonizers, making use of a socalled silent discharge, reaches efficiencies of the order of 5 %.

Although most rate coefficients involved in the ozone formation are available in the literature it seems that no consistent theoretical description of ozone formation in a high pressure discharge has been put forward. Much more effort has been spent on low pressure oxygen discharges which are reasonably well understood (1). While low pressure discharges may be excellent devices to study reaction kinetics they can be ruled out for industrial ozone production because of their mass flow limitations.

2. PROPOSED MODEL

The requirements for reasonable ozone formation can be formulated as follows: The pressure in the discharge should be in the range of 1-2 bar. The gas temperature T_g has to be kept as low as possible to prevent thermal decomposition of ozone. Enough electrons have to be created in the discharge to start the dissociation of O_2 followed by the build-up of O_3. Acceptable ozone concentrations are reached only if volume ionization in the gas provides appreciable electron concentrations. This can only be attained if the E/p-value (electric field strength/pressure), at least temporarily, surpasses the value required for breakdown of the gas (38 V/cm Torr in O_2).

In the following we shall attempt to give a description of the different time scales involved in such a pulsed, spacially homogeneous oxygen discharge at atmospheric pressure. This type of discharge has been called a transient glow because it is characterized by E/p-values typical of glow discharges. It is clear, that, at atmospheric pressure, the transient glow phase with $T_e > T_g$ can last only for a limited time (< 1μs) because collision processes tend to equalize the temperatures. On the other hand, it is observed that discharge instabilities (resulting in sparks or arcs) develop after a certain time and destroy the homogeneity of the discharge. Our description is no longer valid when this occurs. We assume that the discharge is interrupted by external means before the transient glow becomes unstable. Furthermore, no space charge effects are considered at this stage. The dynamics of the discharge is very much influenced by the processes of ionization and dissociative attachment.

$$e + O_2 \xrightarrow{k_1} O_2^+ + 2e \qquad [1]$$

$$e + O_2 \xrightarrow{k_2} O^- + O \qquad [2]$$

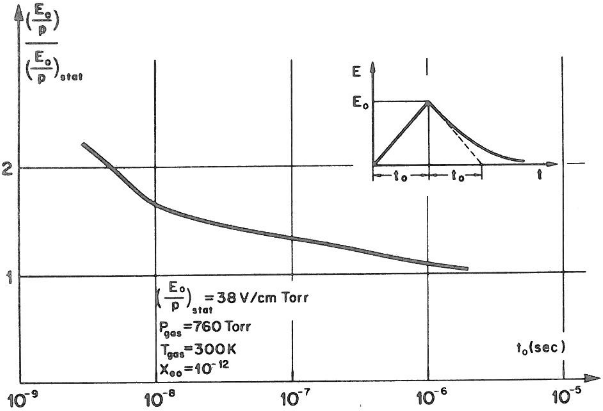

Fig. 1: Maximum peak value of E/p obtainable in oxygen as a function of pulse width.

The rate coefficients k_1, k_2 depend very strongly on E/p (2). At an E/p-value of 38 V/cm Torr the breakdown voltage of oxygen is reached. Most discharges in oxygen are thus limited to the range $0 < E/p < 38$ V/cm Torr. This range of usable E/p-values can be extended if ignition is brought about by a fast rising pulse. From Fig. 1 it becomes apparent that the inherent time lag in the build-up of ionization allows fast rising pulses to reach considerable peak voltages. The curve in Fig. 1 was calculated for a pulse with linear rise to the peak voltage within the time t_0 and an exponential decay with a time constant t_0. Thus, t_0 is roughly the halfwidth of the pulse. Breakdown is assumed to be established if one initial electron has led to the formation of 10^8 electrons. It is further assumed that always enough initial electrons are present in the gap so that no statistical time lag has to be considered. Once the applied pulse falls below 38 V/cm Torr the electrons disappear by attachment with a time constant

$$\tau_e = 1/(k_2 - k_1)\, n_g \qquad [2a]$$

where n_g is the particle density of the gas.

During the rather short life time of the free electrons they react with O_2 and O_3 (if already present)

$$e + O_2 \xrightarrow{k_3} 2O + e \qquad [3]$$

$$e + O_3 \xrightarrow{k_4} O_2 + O + e \qquad [4]$$

k_3 was taken from Ref. 3, k_4 is not well known, but is assumed to be about 5 k_3 (4).

In addition, "chemical" neutral particle reactions occur, the most important of which are:

$$O + O_2 + O_2 \xrightarrow{k_5} O_3 + O_2 \qquad [5]$$

$$O_3 + O_2 \xrightarrow{k_6} O_2 + O + O_2 \qquad [6]$$

$$O + O_3 \xrightarrow{k_7} 2O_2 \qquad [7]$$

$$O + O + O_2 \xrightarrow{k_8} O_2 + O_2 \qquad [8]$$

The coefficients k_5, k_6, k_7 were taken from Benson and Axworthy (5). A discussion of k_8 was given by H. I. Schiff (6). We introduce the particle densities n_1, n_2, n_3, n_e,

n_-, n_+ of O, O_2, O_3, electrons, O^-, and O_2^+ respectively and arrive at the following set of differential equations:

$$\frac{dn_1}{dt} = 2k_3n_en_2 + k_4n_en_3 - k_5n_1n_2^2 + k_6n_2n_3 - k_7n_1n_3 - $$
$$- 2k_8n_1^2n_2 \qquad [9]$$

$$\frac{dn_2}{dt} = -\frac{1}{2}\left(\frac{dn_1}{dt} + 3\frac{dn_3}{dt}\right) \qquad [10]$$

$$\frac{dn_3}{dt} = -k_4n_en_3 + k_5n_1^2n_2 - k_6n_2n_3 - k_7n_1n_3 \qquad [11]$$

$$\frac{dn_e}{dt} = (k_1 - k_2)n_en_2 \qquad [12]$$

$$\frac{dn_+}{dt} = k_1n_en_2 \qquad [13]$$

$$\frac{dn_-}{dt} = k_2n_en_2 \qquad [14]$$

This set of equations was integrated by a Runge-Kutta formalism. For a certain arbitrary voltage pulse the formation of the different species concentrations is plotted in Fig. 2. It becomes evident that the free electron population has a fairly short life span (roughly 5 ns for this pulse) due to the electronegative character of oxygen. The ions O^- and O_2^+, as well as atomic oxygen O are formed rather fast, while the build-up of the ozone concentration takes about 1 - 10 microseconds. Thus, there is little danger of ozone destruction by process (4). One can also conclude from Fig. 3 that each electron has created about 870 O_3-molecules and that there is fairly little loss of atomic oxygen by processes [7] and [8] because the O_3 concentration X_3 reaches about the same height as the concentration X_1.

Integration of the power of the electron and ion current over the pulse length leads us to assess the electrical energy dissipated in the discharge. This allows us to define a figure of merit: the amount of ozone produced per unit of energy used.

Our model predicts that this figure of merit depends very strongly on the pulse shape and pulse height and that it has an increasing tendency towards shorter pulses (Fig. 3).

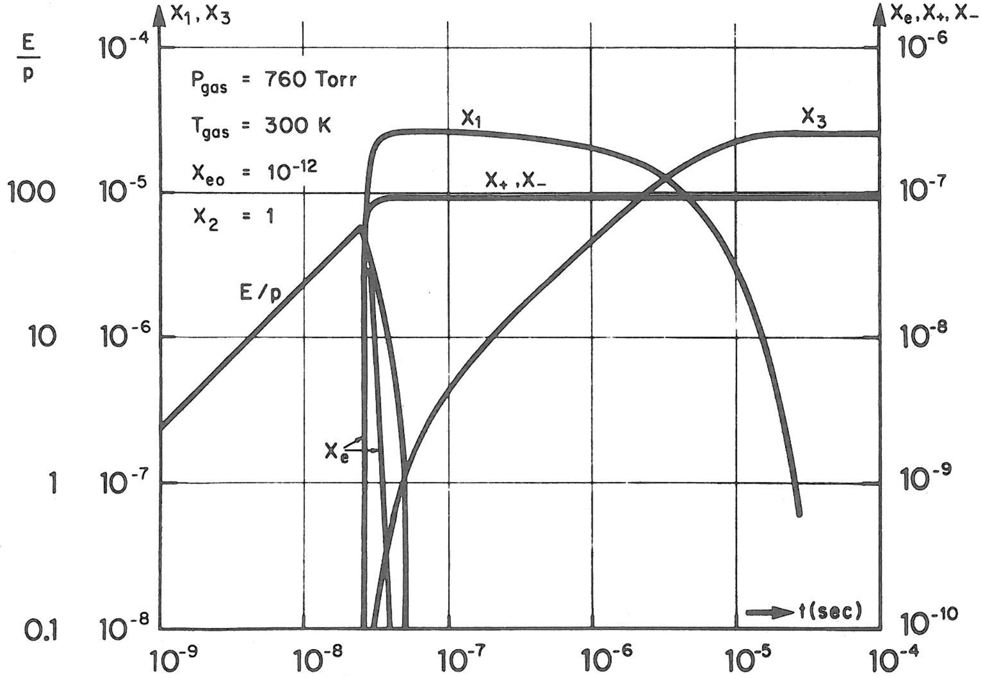

Fig. 2 : Evolution of particle concentrations for a fast applied pulse of indicated shape. (The subscripts e,1,2,3,+,- refer to electrons, $0,0_2,0_3,0_2^+,0^-$ respectively. E/p is given in V/cm Torr).

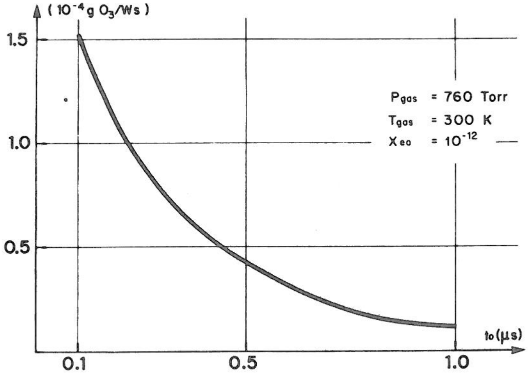

Fig. 3: Specific ozone yield as a function of pulse width.

The model permits the optimization of the pulse shape with respect to the desired ozone concentration and maximum efficiency.

It may be interesting to point out in this connection that the pulsed homogeneous oxygen discharge is not a purely theoretical notion. Experiments with this discharge type have been performed by Braumann and Salge (7) and by Rosocha and Fitzsimmons (8) and have, indeed, yielded high ozone efficiencies.

REFERENCES

(1) H. Sabadil, Beitr. Plasmaphys. 11, 53 (1971)
(2) P. Laboire, J. Rocard and J. Rees, "Electronic Cross-Sections and Macroscopic Coefficients", (2 vols, Dunod, Paris 1968, 1971)
(3) A. T. Bell, Ind. Eng. Chem. Fund 10, 373 (1971)
(4) V. G. Samoilovich, M. P. Popovich, Yu. M. Emalyanov and Yu. V. Philipov, Russ. J. Phys. Chem. 40, 287 (1966)
(5) S. W. Benson and A. E. Axworthy, J.Chem. Phys. 42, 2614 (1965)
(6) H. I. Schiff, Can. J. Chem. 47, 1903 (1969)
(7) P. Braumann and J. Salge, paper, this conference
(8) L. A. Rosocha, W. A. Fitzsimmons, Paper MB-2, 31st Ann. Gas. Electron. Conf., Buffalo, New York, Oct. 17 - 20, 1978.