# STUDY OF OZONE PRODUCTION BY NEGATIVE CORONA DISCHARGE IN MIXTURES OF OXYGEN WITH SOME CHLORINATED METHANES

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## 1. Introduction

The interesting of ozone reactions with specific group of halogencarbons - freons (CFC), has been the focus of numerous kinetic studies in chemistry as well as in plasma [1 - 5]. To our knowledge there are only a few studies on the effect of CFC on ozone production in DC corona or barrier discharges [6 - 13]. Various mechanisms were proposed to explain observed phenomena, sometimes contradictious.

The primary goal of the present work is to study the influence of $CH_xCl_y$ impurities on the process of the ozone generation by DC negative corona discharge in oxygen and to find the main mechanism responsible for the deterious effect of such compounds on the ozone generation.

## 2. Apparatus

All of our experiments were performed using the earlier described [11, 14, 15], modified version of the corona discharge apparatus. The coaxial cylindrical system of the inner and outer electrodes having diameters 0.1 mm and 15 mm respectively, was used. The discharge has been operated at regular intervals lasting eight seconds. After each of these, the ozone concentration was determined by UV light absorption technique [16]. All experiments were carried out at a constant pressure of gaseous mixture of 900 mbar and ambient temperature. The effect of three diluent gases $CH_2Cl_2$ , $CHCl_3$ and $CCl_4$ has been studied.

## 3. Results and discussion

Figs. 1-3 show plots of the time dependent ozone concentration $[O_3]$ in series of five intervals with various $CH_xCl_y$ compounds and at various concentrations of these. It is evident from presented plots, very similar to those reported earlier [13] that :

(i) as the concentration of the diluent gas increases the ozone concentration decreases,

(ii) the more substituted chlorine atoms in the methane molecule are, the more intensive reduction of ozone concentration is observed.

The kinetics of ozone generation by corona discharge in pure oxygen can be restricted to five basic reactions already considered in [17].

**I. Production of oxygen atoms**

R1 $e + O_2 \longrightarrow e + O(^3P) + O(^3P)$ $k_1$

$\longrightarrow e + O(^1D) + O(^3P)$ $k_1^*$

**II. Conversion of oxygen atoms into ozone**

R2 $O + O_2 + O_2 \longrightarrow O_3 + O_2$ $k_2$

**III. Decomposition of ozone**

R3 $O + O_3 \longrightarrow O_2 + O_2$ $k_3$

R4 $e + O_3 \longrightarrow O_2 + O_2 + e$ $k_4$

$\longrightarrow O^- + O_2$ $k_4^*$

$\longrightarrow O_2^- + O$ $k_4^{**}$

R5 $O_2 + O_3 \longrightarrow O_2 + O_2 + O$ $k_5$

All three former groups of processes can be affected by presence of $CH_xCl_y$ molecules in oxygen.

**The production of oxygen atoms** via R1 can be reduced by additional dissociative electron attachment

R6 $e + CH_xCl_y \longrightarrow Cl^- + CH_xCl_{y-1}$ $k_6$

The possibility of such explanation is supported by mass spectrometric measurements made in TCE [5]. However the submitted explanation can not be accepted as the most likely mechanism of inhibition effect because the changes in experimentally measured ozone concentrations do not correspond to more, than three order differences in values of electron attachment coefficients, corresponding to the tested compounds.

**The conversion of oxygen atoms into ozone** can be influenced by the lost of a part of oxygen atoms due to the reactions of these either directly with added chloromethane molecules or with radicals produced by decomposition processes of $CH_xCl_y$ to be active in discharge [4]. The reactions of $O(^1D)$ atoms with chloromethane impurities are much more faster in comparisson with these where $O(^3P)$ is as a reactant. However, also these reactions can be neglected if concentrations of $CH_xCl_y$ in oxygen are below 5% because $O(^1D)$ atoms are lost preferentially to quenching by molecular oxygen [18]

R7 $O(^1D) + O_2 \longrightarrow O(^3P) + O_2$ $k_7$

There are two others most probable sources of by-products available for reactions with oxygen atoms:

1. The direct dissociation of halomethane molecule by electron impact, similar to the photodissociation of mentioned molecules, producing $CH_xCl_{y-1}$. Recently the data for two following processes consuming O were experimentally determined [19]

R8 $O + CH_2Cl \longrightarrow$ products ( $CHClO$, $CH_2O$, H, Cl) $k_8$

R9 $O + CCl_3 \longrightarrow$ products $k_9$

2. Taking into account the results following from theoretical calculations[20], and supposing that $O^-$, $O_2^-$ are the dominant in the drift region of the negative corona discharge generated in

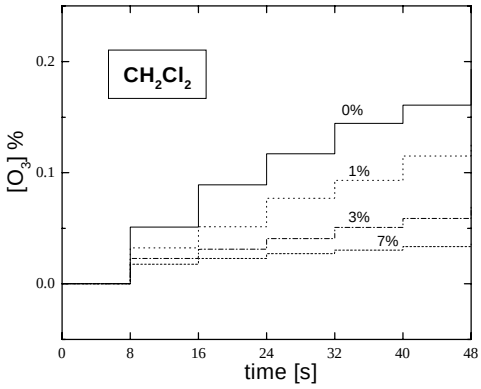


**Figure 1.**

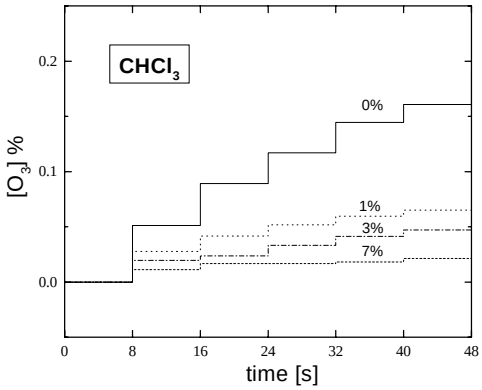


**Figure 2.**

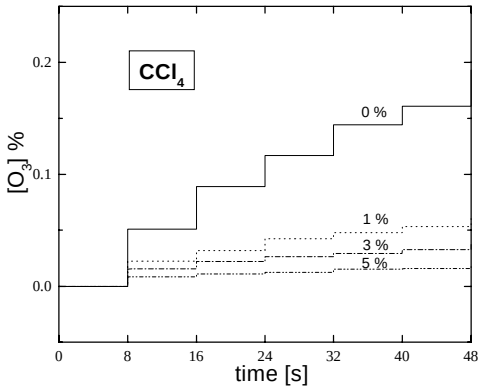


**Figure 3.**

pure oxygen, the generation of various by-products can be expected in gas phase reaction of $O^-$ and $O_2^-$ ions with organic additives in oxygen [21]. The reactions of $O^-$ as well as $O_2^-$ with $CH_2Cl_2$, $CHCl_3$ and $CCl_4$ are very fast, having the rate constants within the interval ( 1.1 - 2.3)x$10^{-9}$ $cm^3.s^{-1}$. The idea, that all parental ions $O^-$, $O_2^-$ are converted to the negative chlorine ions is supported by recently published mass spectrometric study of ions extracted from negative corona discharge initiated in mixtures of air with trichlorelthylene (TCE) [5]. The reactivity of ions $Cl^-$ with ozone is low, but due to the detachment of electrons via the collisions with oxygen atoms, especially in $O(^1D)$ state

R10 $Cl^- + O \longrightarrow e + ClO$ $k_{10}$

the reactive ClO oxides are produced [3]. The $Cl^-$ ions are also produced in collisions of $O^-$ and $O_2^-$ ions mainly in the drift region of the discharge with $CH_xCl_y$ molecules

R11 $O^- + CH_xCl_y \longrightarrow Cl^- + \text{products}$ $k_{11}$

R12 $O_2^- + CH_xCl_y \longrightarrow Cl^- + \text{products}$ $k_{12}$

and therefore the reactions R11, 12 followed by R10 are the source of reactive chlorine oxide ClO.

Besides of already mentioned neutral and ionic product discussed above, the reactions R11, 12 produce very reactive atoms, radicals or reactive by-products [21], mostly very reactive like Cl, ClO and OH The possible exoergic pathway are discussed in [21]. We suppose that among them Cl and ClO are the most important to be responsible for inhibition of process of ozone production, because the portion of oxygen atoms needed for generation of ozone is consumed by the chlorine oxides

R13 $O + ClO \longrightarrow Cl + O_2$ $k_{13}$

producing very reactive chlorine atoms efficiently destroying molecules of ozone

R14 $O_3 + Cl \longrightarrow ClO + O_2$ $k_{14}$

On the account of foregoing qualitative discussion, the set of reactions dominated to the processes of ozone generation and the destruction was selected. The corresponding system of simplified two differential equations was solved giving the time dependence of the ozone concentration in the reactor. The system of reactions and details regarding the solutions will be presented [22]. The exponential increase of the ozone concentration, similar to the Becker's relation [23] and very fast stabilisation of [O] concentration follows from the model [24]. Furthermore, the saturated value of ozone concentration is inversely proportional to the concentration of $CH_xCl_y$ in the mixture and to the summary rate constant characterising all processes in which oxygen atoms are consumed by the by-products of the $CH_xCl_y$ impurities present in oxygen.

Therefore we dare to make a conclusion, that the inhibition of the ozone production observed when ozone is generated by the negative corona discharge in oxygen containing the chloromenthane impurities is a multicomplex process, in which the consumption of the oxygen atoms by the by-products of the decomposition of chloromethane impurities directly in the discharge gap plays the dominant role.

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