Effect of Oxygen Percentage on the Removal of Acetaldehyde by Dielectric Barrier Discharge

O. Koeta\textsuperscript{1, 2}, N. Blin-Simiand\textsuperscript{1}, S. Pasquiers\textsuperscript{1}, F. Jorand\textsuperscript{1}, and A. Bary\textsuperscript{2}

\textsuperscript{1}Laboratoire de Physique des Gaz et des Plasmas, CNRS et Université Paris Sud, France
\textsuperscript{2}Laboratoire de Chimie Analytique de Radiochimie et d’Electrochimie, Université de Ouagadougou, Burkina Faso

Abstract—This work focuses on the effect of oxygen percentage on the conversion of acetaldehyde by dielectric barrier discharges in \textit{N}_2/\textit{O}_2/\textit{CH}_3\textit{CHO} (below 1000 ppm) mixtures, at atmospheric pressure, at 20°C and 300°C. For energy values below 50 J/L the acetaldehyde conversion follows an exponential decrease, for higher values the removal is more efficient. The conversion is efficient in nitrogen but the efficiency increases since 1% of oxygen is added in the mixture and then appears to be independent of oxygen percentage. The conversion increases with the temperature. By-products issued from the conversion are identified. Experimental results emphasize that dissociation of \textit{CH}_3\textit{CHO} by quenchings of \textit{N}_2 metastable states are important processes, even in mixtures containing oxygen.

Keywords—Acetaldehyde, dielectric barrier discharge, dissociation, VOC

I. INTRODUCTION

Acetaldehyde is a Volatile Organic Compound (VOC). This pollutant is found both in indoor air, coming from building materials, and in exhaust gases of ethanol combustion or incinerators. The reduction of the emissions of dangerous substances, like VOCs, passes by the development of effective and economically successful processes of clean-up. In the field of the treatment of air pollution, various technologies already exist like pyrolysis or catalytic oxidation but they require a high consumption of energy. Alternative techniques, as non-thermal equilibrium plasmas at atmospheric pressure are the subject of numerous researches [1-3]. It is in particular necessary to lead fundamental studies to understand the physico-chemical processes involved in the conversion of pollutant molecules by those plasmas. Few studies were made about the conversion of acetaldehyde by filamentary plasmas of dielectric barrier [4-6] or corona discharges [7, 8]. In a previous work, first results were obtained concerning the removal of this aldehyde in nitrogen by a dielectric barrier discharge (DBD) [9]. The purpose of the present work is to better understand kinetics involved in oxidation processes. This is the reason why this work focuses on the effect of low oxygen percentage (up to 10%) on the conversion of this pollutant by DBD in nitrogen/oxygen mixtures at 20°C and at 300°C. This last condition is closed to those observed in exhaust gases of ethanol combustion where acetaldehyde is present. Identification of by-products is made to better understand conversion mechanisms. Accurate relative importance of kinetic processes cannot be easily determined due to the strongly non-homogeneous character of the discharge studied. Therefore our kinetic analysis remains qualitative.

II. EXPERIMENTS

The plasma is produced in a cylindrical DBD (Pyrex tube) already described [9]. Two central tungsten HV electrodes were successively used with either a 2 mm or a 5 mm rod diameter. The energy is provided by a pulsed high voltage generator working at a repetition frequency up to 200 Hz.

A constant gas flow of \textit{N}_2/\textit{O}_2/\textit{CH}_3\textit{CHO} mixture is used (1 l/min NTP), with a constant feed acetaldehyde concentration of 500 ppm or 860 ppm and \textit{O}_2 concentration ranging from 0% to 10%. The plasma volume is 21 cm\textsuperscript{3}. Studies are performed at two temperatures: 20°C and 300°C controlled by a thermoregulated oven. The electrical energy deposited in the DBD is determined through measurements of the voltage and current time evolutions, using adapted electrical probes connected to a fast digital oscilloscope (Lecroy LT584, 1 GHz, 4 GS/s). The applied voltage pulse has a total increase time (from 0 V) of 500 ns, with an increase between 5 kV up to the discharge breakdown (around 22 kV at 20°C, 16 kV at 300°C) in about 55 ns. The specific energy, \( E_s \), is simply determined by

\[
E_s = \nu E_{\text{pulse}}/F, \quad (1)
\]

In Eq. (1) \( E_{\text{pulse}} \) is the deposited energy in the plasma volume per current pulse, \( \nu \) is the pulse frequency, and \( F \) is the gas flow. A 40 kV voltage pulse on a purely capacitive load is applied for all experiments and the specific deposited energy is varied by changing the repetition frequency, \( \nu \). \( E_{\text{pulse}} \) ranges from 54 mJ up to 57 mJ at 20°C and from 86 mJ up to 97 mJ at 300°C. It depends weakly of the gas mixture composition, the temperature, and the frequency.

FTIR analysis and micro-gas chromatography with a thermal conductivity detector (GC-TCD Varian CP 490, columns CP-Sil 5 CB and Molsieve 5Å), and gas chromatography coupled to mass spectrometry (GC-MS Varian Saturn 2000-CP3800 with a column Porabond Q

Corresponding author: Nicole Blin Simiand
e-mail address: nicole.simiand@u-psud.fr

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25 m × 0.25 mm × 3 µm) were used to completely characterize the gas mixture issued from the DBD-reactor in the late afterglow.

III. RESULTS

A. Acetaldehyde Removal

The acetaldehyde concentration was measured at the exit of the DBD reactor for various oxygen percentages in the mixture. An example of the evolution of this concentration, \(C_{\text{exit}}\), as a function of the specific energy is given in Fig. 1 at \(T = 300°C\) for conversion in nitrogen and in nitrogen/oxygen 90/10 mixture.

As already shown [9], the removal of acetaldehyde is efficient, even in absence of oxygen, but it increases when oxygen is added in the mixture as observed in Fig. 1. This positive effect of oxygen on the removal of acetaldehyde was already observed in case of homogeneous transient plasma in a photo-triggered discharge [10] and in a corona discharge in a wire to cylinder configuration [11]. Furthermore \(C_{\text{exit}}\) exhibits an exponential decrease for specific energies \(E_s\) lower than 150 J/L in case of nitrogen and 50 J/L when 10% of oxygen is added. This phenomenon is observed whatever the oxygen concentration. We can write

\[
C_{\text{exit}} = C_0 \exp (-E_s/\beta) \quad (2)
\]

where \(C_0\) is the acetaldehyde inlet concentration, and \(\beta\) is the characteristic energy.

For higher specific energies, \(C_{\text{exit}}\) is lower than the value given by Eq. (2), the removal is more efficient. This effect could be explained by an additional heating of the gas mixture due to the discharge itself.

In Fig. 2 are plotted values of characteristic energies established for each oxygen percentage at 20°C for the 2 mm electrode rod and at 300°C for the two rods (2 and 5 mm). As already shown [9], acetaldehyde removal by the HV-pulse energized DBD is efficient in nitrogen. However, since 1% of oxygen is present in the mixture, the characteristic energy decreases (more than 50%) and appears nearly independent of oxygen percentage, except for 2% which seems to be a particular case for both temperatures. For each oxygen percentage, the evolution of the removal of acetaldehyde was studied as a function of temperature. \(\beta\) decreases when the temperature increases from 20°C to 300°C, showing a better efficiency, as already observed for acetaldehyde and other molecules [12-14]. This is illustrated by Fig. 2 which exhibits also differences between characteristic energies obtained with the 2 mm rod and the 5 mm rod electrodes. This may probably be due to the influence of the radius on the local field inducing differences in the energy distribution in the discharge.

The type of discharge used plays an important role in the energy efficiency for the removal of VOCs. In a previous work using a wire-to-cylinder corona discharge powered by a Marx generator, with similar current pulse characteristics than in our experiment, it was also found that \(C_{\text{exit}}\) decreases exponentially for \(E_s\) lower than 150 J/L, at \(C_0 = 500\) ppm and ambient temperature [11]. However the values of the characteristic energy, \(\beta\), are different than those founds in the present work.

For example, at ambient temperature and for an initial concentration of acetaldehyde \(C_0 = 500\) ppm, with the corona discharge, the value of characteristic energy is \(\beta = 160\) J/L in nitrogen and 125 J/L in nitrogen with 5% of oxygen. These values are a factor of two lower than the characteristic energies found in the present work for the DBD reactor, under the same conditions of concentration and temperature. Such a difference on the \(\beta\) values, established between corona and DBD reactors, should be related to different spatial distribution of the deposited energy in the discharge volume. Considering the temperature dependence of the characteristic energy found for different VOCs and discharge types, the comparison between characteristic energies for different plasma reactors makes sense only if the gas temperature in the discharge volume is known, taking into account heating of the gas by the discharge. In case of a negligible heating effect, the importance of the energy...
distribution has been also pointed out for 2-heptanone diluted in dry air by comparison between excitation by an alternating current and a pulsed discharge for a DBD in N₂ and N₂/O₂ mixtures [15].

B. By-products in N₂/acetaldehyde Mixtures

In the N₂/CH₃CHO mixture plasma, the main products are CO, CO₂, HCN, HNCO, HONC, CH₄, C₂H₆ detected by FTIR and H₂ detected by GC-TCD. Furthermore, CH₃CN and traces of C₂N₂, C₂H₆CN, C₃H-CN, CH₂COCH₂, CH₃C(O)OC(O)CH₃ (acetic anhydride) were identified by GC/MS.

The most abundant by-product is CO, followed by hydrogen and methane in equivalent amounts, then ethane and hydrogen cyanide (HCN). Very low concentration of carbon dioxide and formaldehyde (below 10 ppm) are also observed. Those by-products are the proof of dissociation of acetaldehyde molecule in nitrogen [9, 10].

The efficient production of hydrogen at 300°C is illustrated by Fig. 3. H₂ concentration increases linearly with the energy, then saturates and decreases for specific energies above 200 J/L.

As for other VOCs, electrons and N₂ metastable states should be involved in the removal of acetaldehyde in nitrogen, i.e.

\[ e^- + CH₃CHO \rightarrow \text{products} + e^- \]  
\[ N₂(A^3Σ_u^+) + CH₃CHO \rightarrow \text{products} + N₂ \]

Nitrogen metastable states are probably more important than electrons owing to their higher lifetime. In a recent work, the following dissociation channels were proposed with a global reaction coefficient \( k = 5.5×10^{-11} \text{ cm}³/\text{s} \) [10].

\[ N₂(A^3Σ_u^+) + CH₃CHO \rightarrow CH₃ + HCO + N₂ \]  
\[ N₂(A^3Σ_u^+) + CH₃CHO \rightarrow CH₄ + CO + N₂ \]  
\[ N₂(A^3Σ_u^+) + CH₃CHO \rightarrow CH₂CO + H₂ + N₂ \]

This scheme is in good agreement with the identification of H₂, CO, CH₄ as major by-products. Furthermore the following reactions (see also Table I) can also explain the formation of those species:

\[ \text{HCO} + \text{HCO} \rightarrow \text{CO} + \text{CH}_₂\text{O} \]  
\[ \text{HCO} + H \rightarrow \text{CO} + \text{H}_₂ \]  
\[ H + \text{CH}_₃ + N₂ \rightarrow \text{CH}_₄ + N₂ \]  
\[ N + \text{CH}_₃ \rightarrow \text{HCN} + H₂ \]

(R9) is also a channel explaining the formation of HCN. Reactions of CH₃ radicals lead also to ethane:

\[ \text{CH}_₃ + \text{CH}_₃ + N₂ \rightarrow \text{C}_₂\text{H}_₆ + N₂ \]

Reaction (R6) generates formaldehyde observed in low amounts because of its treatment by the discharge which was already shown to be efficient [14].

The increase of the conversion of acetaldehyde in nitrogen with increasing temperature should be partly assigned to (R2). Actually, it was already shown for methane and ethane that the quenching coefficient of N₂(A³Σ_u) by an hydrocarbon increases as the temperature increases [16]. It is also probably the case for aldehydes.

C. By-products in N₂/O₂/acetaldehyde Mixtures

The addition of oxygen modifies by-products issued from acetaldehyde conversion. In this case, FTIR allows to identify CO, CO₂, HCN, H₂O, formaldehyde (CH₂O), formic acid (HCOOH), methanol (CH₃OH), acetic acid (CH₃COOH), methyl nitrate (CH₃ONO₂) (at 20°C), peroxyacetyl nitrate (PAN: CH₃(C(O)OONO₂) (at 20°C), HNO₃, NO (at 300°C), NO₂ (at 300°C), N₂O₃ (at 20°C), N₂O and O₃ (at 20°C). Analysis by GC/MS lead to detect CH₃NO₂ and traces of methyl acetate (CH₃C(O)OCH₃), butanal (C₃H₇CHO), pentanal (C₅H₉CHO) and hexanal (C₆H₁₁CHO). The identification of some by-products by FTIR is illustrated by Fig. 4.
When oxygen is added to the mixture, quenchings of nitrogen excited states produce oxygen atom \( O(3P) \), for example:

\[
\text{N}_2(A^3\Sigma^+ + u) + O_2 \rightarrow O(3P) + O(3P) + N_2 \quad (R11)
\]

These quenchings entail a decrease of the dissociative reactions \((R2)\) and a competition appears, at low oxygen concentrations, for the removal of acetaldehyde between dissociation processes \((R3)-(R5)\) and oxidation reactions \((R12)-(R13)\) (see Table I):

\[
\text{O}(3P) + \text{CH}_3\text{CHO} \rightarrow \text{OH} + \text{CH}_3\text{CO} \quad (R12)
\]
\[
\text{OH} + \text{CH}_3\text{CHO} \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{CO} \quad (R13)
\]

The oxidation of \( \text{CH}_3\text{CHO} \) compensates for the decrease of dissociative reactions and explains the rapid decrease of characteristic energy since a little amount of oxygen is added to the mixture.

In oxygen containing mixtures, the increase of the acetaldehyde removal efficiency when the temperature increases should be related to the increase of the efficiency of oxidation reactions \((R12)\) and \((R13)\) (see Table I):

\[
\text{O}(3P) \rightarrow \text{OH} \rightarrow \text{CH}_3\text{CO} \rightarrow \text{CO} + \text{CH}_2\text{O} \quad (R14)
\]

where the hydrogen atom should come from the dissociation of \( \text{CH}_3\text{CHO} \) by \((R1)\) and \((R2)\).

The comparison of oxidation coefficients, set on Table I, shows that coefficient for reactions \((R12)\) is an increasing function of \( T \) but remains much lower than the coefficient for \((R13)\) as it can be observed in Fig. 5.

Therefore the role of \( \text{OH} \) in the conversion of acetaldehyde by the DBD reactor is probably important at low temperature even if the inlet mixture does not contain water molecule.

Figs. 6 and 7 show the concentration of by-products identified in mixtures containing 5\% of oxygen at respectively 20\(^\circ\)C and 300\(^\circ\)C. Solid lines correspond to fit of linear increase of by-products concentration with energy. Some by-products are observed to be treated by the discharge, like formaldehyde, methanol and, to a lower extent, methane. This treatment is symbolized by dash lines. This phenomenon is more visible at 300\(^\circ\)C where a slight treatment of \( \text{H}_2 \) and \( \text{CO} \) is also observed. At 20\(^\circ\)C a few amount of \( \text{HCN} \) shows that dissociation reactions compete with oxidation.

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In order to explain the formation of by-products, oxidation of acetyl radical has to be taken into account:

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\text{CH}_3\text{CHO} + \text{O}_2 \rightarrow \text{CO} + \text{CH}_2\text{O} \quad (R14)
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The comparison of oxidation coefficients, set on Table I, shows that coefficient for reactions \((R12)\) is an increasing function of \( T \) but remains much lower than the coefficient for \((R13)\) as it can be observed in Fig. 5.
Then the kinetics of CH$_2$CO produces H, HCO, CH$_3$OH, CO, and CH$_2$O.

(R15) is an important source for the methyl radical. Another source for this radical is reaction:

\[ \text{HO}_2 + \text{CH}_3\text{CO} \rightarrow \text{CH}_3 + \text{CO}_2 + \text{H} \quad (R18) \]

with \( \text{HO}_2 \) issued from:

\[ \text{H} + \text{O}_2 + \text{N}_2 \rightarrow \text{HO}_2 + \text{N}_2 \quad (R19) \]

Oxidation of methyl radical leads to methyldperoxy radical:

\[ \text{O}_2 + \text{CH}_3 + \text{N}_2 \rightarrow \text{CH}_2\text{O}_2 + \text{N}_2 \quad (R20) \]

followed by the production of methoxy radical CH$_3$O:

\[ \text{O}^{(3P)} + \text{CH}_3\text{O}_2 \rightarrow \text{O}_2 + \text{CH}_3\text{O} \quad (R21) \]
\[ \text{H} + \text{CH}_3\text{O}_2 \rightarrow \text{OH} + \text{CH}_3\text{O} \quad (R22) \]
\[ \text{CH}_3 + \text{CH}_3\text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{CH}_3\text{O} \quad (R23) \]
\[ \text{HCO} + \text{CH}_3\text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{CO}_2 + \text{H} \quad (R24) \]
\[ \text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{CH}_3\text{O} + \text{O}_2 \quad (R25) \]

The radical CH$_3$O is also produced by:

\[ \text{HO}_2 + \text{CH}_3 \rightarrow \text{OH} + \text{CH}_3\text{O} \quad (R26) \]

The acetyl radical issued from (R12) or (R13) can lead to the production of acetylperoxy radical:

\[ \text{O}_2 + \text{CH}_3\text{CO} \rightarrow \text{CH}_3\text{C(O)}\text{OO} \quad (R27) \]

Then three-body reactions produce methyl nitrate, CH$_3$ONO$_2$:

\[ \text{NO}_2 + \text{CH}_3\text{O} + \text{N}_2 \rightarrow \text{CH}_3\text{ONO}_2 + \text{N}_2 \quad (R28) \]

or PAN, CH$_3$C(O)OONO$_2$:

\[ \text{NO}_2 + \text{CH}_3\text{C(O)}\text{OO} + \text{N}_2 \rightarrow \text{PAN} + \text{N}_2 \quad (R29) \]

The detection of those molecules strengthens the important production of methyl and CH$_3$CO radicals through either dissociation or oxidation processes of the acetaldehyde.

It can be observed in Fig. 8 that the PAN concentration saturates and decreases when the specific energy increases above 150 J/L. Furthermore, this concentration decreases during time for higher energy value. This effect is probably due to the increase of the temperature in the discharge volume due to the electrical energy deposition until the DBD reactor reaches a thermal equilibrium.

IV. CONCLUSION

The conversion of acetaldehyde is efficient in nitrogen but the efficiency increases significantly since only 1% of oxygen is added to the mixture. The conversion depends on the mixture temperature: it increases with the temperature. By-products issued from the conversion emphasize that, in nitrogen, acetaldehyde is dissociated by collisions with electrons and nitrogen
metastable states. In mixtures containing oxygen, dissociation of CH₃CHO by quenching of N₂ metastable states competes with oxidation reactions.

More quantitative explanations for these effects have to be confirmed by a kinetic modeling.

REFERENCES


