Isotopic GC/MS study to identify the mechanism of acetaldehyde decomposition in a dielectric barrier discharge

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ABSTRACT:

An experimental study on the decomposition of acetaldehyde in dry air mixture has been carried out using plasma chemical reactions to understand the reaction pathways. A point to plane dielectric barrier discharge is used and operating parameters that affect the CH₂CHO destruction efficiency include the gas mixture composition, the applied electric parameters, and the gas residence time in the reactor. Plasma is produced in a narrow gap by a dielectric barrier discharge at low applied 40 kHz voltage. The outlet gas composition is monitored with a gas chromatography coupled to mass spectrometry that allows quantifying the amount of CO, CO₂, volatile organic compounds and alkanes. An isotopic labeling (D and ¹⁸O) is used with GC/MS identification of the formed stabilized species in order to investigate the plasma chemical mechanisms of acetaldehyde decomposition, and especially the oxygen influence. The results imply that O radicals achieve the initial decomposition of acetaldehyde through oxidation. The recombination of CH₃ radicals formed from acetaldehyde is observed in most by-products and confirmed by CD₃ isotopic labeling. This phenomenon is particularly interesting in the case of R-NO₂ formation. This study also suggested that the mass balance was a major information to evaluate the efficiency of the process.

1. Introduction

The purpose of this work is to understand the DBD by-products formation mechanisms using labeling molecules; the following isotopes are D and ¹⁸O. Acetaldehyde is the molecule at stake in this study. This choice is justified for various reasons: this molecule is simple and, further more, a parallel can be drawn between the plasma discharge depollution process and a classical thermal treatment like combustion (CH₃CHO→CH₄+CO₂; 518°C, 1 atm).

The use of the labeled molecules allows distinguishing two reactions bringing to the same product. For example NO and CO reactions on rhodium / cerium catalysts:\n\[N^{¹⁸}O + ^{¹²}C^{¹⁴}O = ^{¹⁸}N₂ + ^{¹²}CO₂\] and \[2N^{¹⁸}O + ^{¹³}C^{¹⁶}O = ^{¹⁸}N₂ + ^{¹³}C^{¹⁶}O^{¹⁸}O⁻\].

We can also conclude on the molecules atomic exchanges, as well as the specific bond cuts and the most likely rearrangements in molecules.

The acetaldehyde methyl function labeled by deuterium (-CD₃) provides us with information about the reaction pathway involving the different radicals produced by the corona discharge. Gas phase chromatography coupled with mass spectrometry analysis leads to a validation of the material balance as well as a good distinction of isotopes ratio.
2. Experimental Set-Up

The figure 1 shows the experimental setting consisting of a point-to-plane reactor connected to a high voltage 40 kHz power supply. The point-to-dielectric barrier distance is 6 mm and the flow rate of the gas mixture (N₂/O₂ + 1.5 % acetaldehyde) is 1 L / min. The electrical parameters were controlled with a numerical oscilloscope LeCroy 500 MHz. A gas chromatography coupled with mass spectrometry (GC/MS) analysis the discharge by-products. The operating parameters of the GC/MS are also summarized below.

![Figure 1](image)

**Figure 1:** Experimental set-up and process controls.

3. Electric discharge control

The electric circuit shown in figure 2 allows the discharge control. A numerical oscilloscope LeCroy 500 MHz has been used to characterize voltage, energy and impulses (frequency, duration, intensity, and energy densities...).

![Diagram](image)

Voltage and current measures are reported in figure 3. The peak to peak voltage and the frequency records are shown in the left figure, the current component bearing the elementary discharge is presented in the right figure. Electrical parameters were controlled in order to be correlated to macroscopic phenomena sustained the discharge area [2].

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4. Identification of reactions pathway using labeling molecules

The reactor exhaust gas composition during the air / acetaldehyde mixture treatment is shown in figures.4. Detected compounds were classified into three reaction families: “combustion” reactions \(\text{C}_x\text{H}_y\text{O}_z \rightarrow \text{CO}_x + \text{H}_2\text{O}\), reactions between a radical and a NO\(_x\): \(\text{R}^\cdot + \text{NO}_x \rightarrow \text{R-NO}_x\), and reactions between other radicals: \(\text{R}^\cdot + \text{R}''^\cdot \rightarrow \text{R-R}''\).

The variety of products getting out of the reactor and identified by GC / MS stems from a preferential bound cut between the aldehyde function and the methyl radical. It is particularly interesting to notice the coupling between the NO\(_x\) produced by \(\text{N}_2\text{O}_2\) discharge \([1]\) and CH\(_3\) radicals, which is revealed through the methyl nitrate (CH\(_3\)-O-NO\(_2\)), methyl nitrite (CH\(_3\)-O-NO) and nitromethane (CH\(_3\)-NO\(_2\)) formation. It allows anticipating the possibility of NO\(_x\) removal using uncombusted hydrocarbons from the vehicle engine exhaust \([4]\).

- Deuterium labeling:
Chemical mechanisms presented in figure 5 summarize a part of the reaction pathway occurring during the CD₃CHO treatment. Unlike the aldehyde hydrogen, the hydrogen atoms belonging to the methyl are not exchanged in our treatment conditions. This conclusion can be drawn through the large presence of the CD₃ radical. Moreover, CD₃ trapping leading to R-NOx compounds can be noticed once again. Formaldehyde (H₃CO) and methanol (CH₃OH) formation illustrates the hydrogen exchanges.

Figure 5.a: CH₃CHO decomposition pathway
Figure 5.b: CD₃CHO decomposition pathway

- Deuterium labeling information

The labeled methyl radical (CD₃) highlights the acetaldehyde decomposition mechanism. The bond between the methyl and the aldehyde function (HC=O) is preferentially cut:

\[
\text{CH₃CHO} \rightarrow \text{CH₃} + \text{CHO} \quad (\text{CD₃CHO} \rightarrow \text{CD₃} + \text{CHO})
\]

The stability of the methyl function does not exclude hydrogen exchanges. For example, formaldehyde, methanol and methane formation (illustrated respectively by the following reaction pathways) is a confirmation to this.

\[
\text{CD₃} + \text{O} \rightarrow \text{CD₃O} \rightarrow \text{D₂C}=\text{O}
\]

1. Formaldehyde production:
Oxygen labeling ($^{18}$O):

The hydrocarbon oxide molecules formed by the corona discharge are chiefly identified in aldehyde and alcoholic functions. Thus, one can distinguish the oxygen atoms belonging to the reacting acetaldehyde from those provided by the air ($N_2/^{18}O_2$).

The chromatogram obtained with the GC/MS analyzer is presented in figure 6. It allows the identification of the by-products discharge. It can be noted that all the methyl nitrate, methyl nitrite, nitromethane, and nitrous oxide ($N_2O$) molecules are exclusively made of the labeled oxygen ($^{18}$O).

![Chromatogram of the DBD reactor exhaust gas composition](image)

*Figure 6: Chromatogram of the DBD reactor exhaust gas composition (Point-plane: d: 6 mm; D: 1L / min; $N_2 + ^{18}O_2 +$ acetaldehyde (1.5%))

The carbonyl function remains exactly the same (no oxygen exchange) except for the formaldehyde ($H_2CO$) and $CO/CO_2$ equilibrium ($C^{16}O_2$: 20%, $C^{16,18}O_2$: 70% and $C^{18}O_2$: 10%). The by-products can be classified as follows:
- Oxygen labeling information

The $^{18}$O atomic coming from (CH$_3$CHO/N$_2$/$^{18}$O$_2$) discharge system is detected in different molecules. It’s preferentially bonded to a methyl radical (-CH$_3$) according to the following reaction:

$$CH_3 + ^{18}O \rightarrow CH_3^{18}O$$

The reaction pathway illustrated below can account for CO$_2$ exchanges and the above-mentioned isotopic distribution.

**Conclusion**

This study was run following two complementary approaches. A first part involved the isotopic labeling of the treated acetaldehyde molecule (CD$_3$CHO) and the air mixture (N$_2$/$^{18}$O$_2$). A second part included plasma chemical mechanisms, and highlighted the effect of the methyl radical on by-products formation, along with the atom exchanges mechanisms within the plasma discharge. The efficiency of the plasma process could then be optimized from the exhaustive monitoring of the gas effluent by GC/MS.

The acetaldehyde transformation process originates in the atomic oxygen produces by the plasma discharge. O$_2$ excitation via electron impacts is the first step of the reactional process triggered by the corona discharge.

The process spreading leads up to chain radical reactions. During those reactions, methyl radical (identified thanks to deuterium) plays a lead part in getting oxygenated organic compounds (alcohol, ether...). On the contrary, oxidation mechanisms of CH$_3$ and CO radicals are the results of multiple oxidation by atomic oxygen. Doubly labeled CO$_2$ gives proof of CH$_3$ oxidation via CO$_2$. 

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References


