Role of Nitrogen Metastable States in Non-Thermal Plasma Conversion of Volatile Organic Compounds

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Abstract— The conversion of formaldehyde and acetaldehyde is studied in N2 and in N2/O2 mixtures energized by a dielectric barrier (filamentary plasma) or a photo-triggered (homogeneous plasma) discharges. In these high pressure non-thermal plasmas and at low temperature, it is shown that the dissociation of these molecules due to collisional quenching of the nitrogen metastable excited states can play a non-negligible role in both mixture types (with or without oxygen). The formaldehyde removal efficiency decreases as soon as some oxygen is added to the mixture. This is not the case for acetaldehyde. A kinetic explanation for this difference is proposed.

Keywords—Formaldehyde, acetaldehyde, quenching of nitrogen metastable states, dielectric barrier discharge, photo-triggered discharge

I. INTRODUCTION

High-pressure, low-temperature plasmas generated in atmospheric gases (N2, O2, H2O, and their mixtures) are widely studied for various applications such as pollution control (removal of VOCs ...) [1, 2], as well as ignition and combustion control [3]. However there is a lack of knowledge about the kinetics involved in such plasmas, in particular dissociation processes of hydrocarbon (HC) and VOC molecules through quenching collisions of the nitrogen metastable electronic states [4]. These states are highly populated in most of non-equilibrium pulsed discharges produced in the N2/O2(H2O) mixture, so that they should play a non-negligible role in the conversion of HC and VOC added to this mixture. This paper gives recent results obtained on aldehydes in our laboratory, either for filamentary plasmas such as those generated by dielectric barrier discharges [5], or homogeneous plasmas produced by pre-ionized (photo-triggered) discharges [6].

The photo-triggering technique allows one to achieve homogeneous transient high-pressure plasmas in various types of gas mixtures and at various total pressure values, (0.1 bar up to several bars). Measurements can be compared with confidence to predictions of a self-consistent 0D discharge and kinetic model which takes into account all relevant reactions for the mixture under consideration. We have used such a discharge and its modelling to study the conversion of propane diluted in nitrogen [7], or to study the kinetics of the hydroxyl radical in the N2/O2 mixture with addition of VOCs (acetone or isopropyl alcohol) [8] or light hydrocarbons (ethene, ethane, propane) [9-11]. In particular it was shown that N2 metastable states (A3Σu+, with an excitation threshold at 6.17 eV, but also singlets: a1Σg+, a1Πg, and w1Δu, with a threshold at 8.4 eV) play an important role in the kinetic chain leading to the production of OH, owing to dissociative quenching collisions of these states on the carbonated molecules. Such processes must be taken into account to explain the degradation of VOCs and hydrocarbons.

Amongst pollutant VOCs for which the removal by non-thermal plasmas deserves to be studied, we have chosen formaldehyde and acetaldehyde. Works were performed both in DBD [12-14] and in pre-ionised discharges [15], for a maximum molecule concentration of 5000 ppm diluted in N2 or in N2/O2 mixtures. All experiments have been performed at ambient temperature (near 20°C). For the filamentary plasma of a DBD, only results about the conversion of formaldehyde are presented and discussed in the present paper.

II. EXPERIMENTS

Two kinds of photo-triggered discharge reactors, hereinafter referred to UV510 [18] and UV2412 [19], were used. A detailed description of these UV-preionized reactors has been previously published [6-10, 16] and it will be not recalled here. The conversion of formaldehyde (resp. acetaldehyde) in N2 and N2/O2 mixtures was studied in UV2412 (resp. UV510), with a homogeneous plasma volume of 58 cm3 (resp. 50 cm3). UV510 allows studying the plasma kinetic following one current pulse excitation of the gas mixture under investigation (for a chosen specific energy: 92 J/l, total pressure: 460 mbars), whereas UV2412 is used to study the multi-pulse effect similarly to DBD-reactors (specific energy: 6.4 J/l for one current pulse excitation, maximum number of pulses: 5, total pressure: 400 mbars).

A DBD reactor was operated in a cylindrical coaxial geometry, the plasma being created at 1 bar for total pressure in a Pyrex tube of 14 mm for inner diameter. The discharge volume was 20 cm3. A stainless steel tape surrounding the dielectric tube was grounded, while a
high voltage pulse was applied on a central tungsten rod (5 mm diameter). The repetition frequency value was chosen up to 100 Hz. 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) in about 55 ns. The specific energy, $E_s$, is simply determined by:

$$E_s = \nu \frac{E_{\text{pulse}}}{F}$$  \hspace{1cm} (1)

where $E_{\text{pulse}}$ is the deposited energy in the plasma volume per current pulse, $\nu$ is the pulse frequency, and $F$ is the volumic flow. All measurements were performed for a constant applied voltage (40 kV on a purely capacitive load), and the specific deposited energy was varied by changing the frequency. The energy per pulse decreased weakly from 65 up to 55 mJ when the frequency was increased from a few Hz up to 100 Hz.

FTIR absorption spectroscopy and various gaseous chromatographic techniques (GC-TCD, GC-FID, GC-MS) were used to measure the removal of the pollutant molecule, and to identify by-products and quantify their concentrations. GC-TCD was also used to ensure that all reactors (with a photo-triggered discharge or with a DBD) were free from air leaks (no oxygen detected in the introduced nitrogen based gas mixture).

III. SELF-CONSISTENT MODELING

For photo-triggered discharge reactors, experimental results were compared to predictions of a self-consistent 0D modeling of the discharge and of the plasma kinetic. This model couples: (i) the solution of the Boltzmann equation for the electrons, (ii) the kinetic equations describing the temporal evolution of the various species (molecular excited states, ions, atoms, radicals, molecules) produced during the discharge or during the afterglow, and, (iii) the electric circuit equations given by the Kirchhoff laws. The gas temperature time evolution is taken into account through the resolution of the energy conservation equation.

The model has been described in detail previously, together with the kinetic scheme adopted for the nitrogen and oxygen molecules [6, 9]. For these molecules, the excited species correspond to effective states clustering real molecular levels. Details about molecular excited states and cross sections taken into account are given in [9], and references therein. The kinetic of the N$_2$/O$_2$ mixture includes electron collisions on molecules, negative and positive ions reactions (recombination and charge transfers), $v$-$v$ and $v$-$T$ processes of N$_2$, radiative de-excitation and quenchings of excited states, excitation transfers, radical and molecule reactions. Based on the existing literature, all known reactions for ozone were considered in our modeling.

For all compounds of the mixtures, coefficients for electron collisions are directly obtained from the solution of the Boltzmann equation. Those for reactions between the heavy species (neutrals and ions) are taken in great part from a critical review of various compilations and from databases [4, 19-21].

Specifically for the UV2412 reactor, a multi-pulse model allows us to describe the effect of electrical energy deposition when the gas mixture is not entirely renewed in the discharge gap between two successive current pulses. For each pulse, the inputs for this model are the species densities predicted by the self-consistent one 500 ns after the discharge, with the addition of some residual molecule density values coming from the afterglow of the preceding pulse.

IV. FORMALDEHYDE REMOVAL

A. Experimental results for filamentary plasma

In figure 1 is plotted typical experimental results obtained for the removal of CH$_2$O by the DBD-reactor. For this example the initial concentration diluted in N$_2$ or in synthetic air (20 % O$_2$), C$_0$, is equal to 300 ppm.

![Fig. 1. Removal of 300 ppm formaldehyde in N$_2$ and N$_2$O$_2$ filamentary plasmas at 1 bar. Dashed lines are fit of experimental points at low energy values.](image)

For various gas mixtures, type of VOC and discharge, it has been shown in the literature [22-24] that the exit concentration, C$_{\text{exit}}$, is given by,

$$C_{\text{exit}} = C_0 \exp(-E_s / \beta)$$  \hspace{1cm} (2)

on a large range of specific energy values, where $\beta$ is called the characteristic energy. In our experiment with formaldehyde, as previously emphasized for a lower C$_0$ value, 150 ppm [12], the decrease of C$_{\text{exit}}$ does not exhibit a single exponential behavior when the specific energy increases. Dashed lines in figure 1 are fit of experimental points using (2) for $E_s$ less than 75 J/l. For high energy values, C$_{\text{exit}}$ is lower than the concentration given by (2); such a behavior was encountered for all C$_0$ values studied. However the most important result is that the removal of CH$_2$O is more efficient in nitrogen than in air: $\beta = 100$ J/l for N$_2$ whereas $\beta = 160$ J/l for 20 % of oxygen in the gas mixture. In fact, we have established
that, for a given specific energy value, the addition of a small quantity of oxygen leads to increase the characteristic energy (and so to decrease the removal efficiency) with respect to the value measured for the nitrogen plasma.

The results plotted in the figure 1 emphasizes that formaldehyde is efficiently decomposed in the nitrogen plasma. It leads to the production of the following compounds: CO, CO₂, H₂, CH₄, HCN, and HNCO. In figure 2 are plotted concentrations of hydrogen and of carbon oxides, for the same conditions than for figure 1. Concentrations of CH₄, HCN and HNCO are below 20 ppm on the whole range of C₀ values studied.

Fig. 2. Concentration of by-products at the exit of the DBD-reactor, for 300 ppm of formaldehyde diluted in N₂.

Concentrations of CO and H₂ are almost equal and increase linearly when the specific energy increases. It is also the case for CO₂, but the corresponding concentration is much lower. Clearly CH₃O is dissociated by collisions with electrons,

\[ e^- + CH₂O \rightarrow \text{products} + e^- \]  

(R1)

and most probably by collisional quenching of the nitrogen electronic metastable states,

\[ N₂(\text{a}') + CH₂O \rightarrow \text{products} + N₂ \]  

(R2)

\[ N₂(\text{a}'') + CH₂O \rightarrow \text{products} + N₂ \]  

(R3)

where N₂(\text{a}') denotes the group of singlet states (\text{a}' 1\Sigma_u^+, \text{a}' 1\Pi_g \text{ and } \text{w} 1\Delta_o). The metastable states should have the more important role in the formaldehyde dissociation process, owing to their higher lifetime in the discharge afterglow, as compared to other excited (radiative) states of N₂.

The lowest binding energy in the formaldehyde molecule is for the C–H bond, equal to 3.71 eV following calculations performed with the 6-311G(d,p) basis set and using the B3LYP theoretical method [25]. Moreover the transition energy of the first electronic excited state (the triplet 1 Λ₂) is between 3 and 4 eV [26]. Therefore, energies of N₂(1 Σ_u⁻) and of the singlet states are high enough to excite and then to dissociate CH₂O. In fact the dissociation of the collision partner with N₂(1 Σ_u⁻) has been observed for several molecules and it has been measured to be the dominant channel for numerous compounds [4]. Golde [27] argued that there is only one mechanism for quenching, electronic to electronic energy transfer to an excited state of the collision partner, which can then decompose. The results plotted in figure 2 strongly suggest that the main dissociation route for the quenching of N₂(1 Σ_u⁻) by formaldehyde can be,

\[ N₂(1 Σ_u⁻) + CH₂O \rightarrow H₂ + CO + N₂ \]  

(R4a)

However two other channels should also take place,

\[ N₂(1 Σ_u⁻) + CH₂O \rightarrow H + HCO + N₂ \]  

(R4b)

\[ N₂(1 Σ_u⁻) + CH₂O \rightarrow H + H + CO + N₂ \]  

(R4c)

followed by several processes explaining the formation of hydrogen and carbon monoxide,

\[ H + H + N₂ \rightarrow H₂ + N₂ \]  

(R5)

\[ H + HCO \rightarrow CO + H₂ \]  

(R6)

\[ HCO + HCO \rightarrow CH₂O + CO \]  

(R7)

\[ H + CH₂O \rightarrow HCO + H₂ \]  

(R8)

The minimum energy for the production of two hydrogen atoms, reaction (R4c), is low: 4.59 eV [25]. Therefore this dissociation path cannot be ruled out.

Electrons should also participate to the dissociation of the molecule, reaction (R1), but only during the short current pulse of the discharge (100 ns). According to published data on UV-photodissociation processes [28], products could be those given by (R4a) and (R4b).

Reactions similar to (R4a-R4c) can be proposed for the quenching of N₂ singlet states. Besides, a few amount of CO₂ is detected. This compound is a product of reactions involving the oxygen atom, and for the mixture under investigation the most probable processes should be,

\[ O(3P) + CO + N₂ \rightarrow CO₂ + N₂ \]  

(R9)

\[ O(3P) + HCO \rightarrow CO₂ + H \]  

(R10)

Two processes can lead to the oxygen atom: firstly,

\[ N + HCO \rightarrow O(3P) + HCN \]  

(R11)

and secondly, the quenching collisions of the singlets by formaldehyde,

\[ N₂(\text{a}') + CH₂O \rightarrow O(3P) + CH₂ + N₂ \]  

(R12)

Indeed, the energy for the double bond C=O is 7.61 eV [25], i.e. it is lower than the energy of singlets. Also, the detection of CH₄ proves that (R12) is involved in the removal of CH₂O. First, the methyl radical is created by,

\[ CH₂ + HCO \rightarrow CH₃ + CO \]  

(R13)

\[ CH₂ + CH₂O \rightarrow CH₃ + HCO \]  

(R14)
and then,
\[ H + CH_3 + N_2 \rightarrow CH_4 + N_2 \]  \hspace{1cm} (R15)

Reactions (R8) and (R14) participate to the removal of CH$_2$O, but it is less efficient than the reaction (R7) for the creation of the molecule at low temperature [19, 20].

Suzuki et al. [29] have measured the coefficient for the reaction (R2)-(R4), \( k_{R4}=4.7\times10^{-12} \text{ cm}^3\text{s}^{-1} \). Moreover the coefficient for the quenching of singlet states, \( k_{R3} \), should be higher than the one for \( \Lambda^\Sigma_u^+ \), as previously demonstrated for light hydrocarbons [7, 10, 30]: for ethene, the coefficient for the (R2)-type reaction is \( 1.1\times10^{-10} \text{ cm}^3\text{s}^{-1} \) for \( \Lambda^\Sigma_u^+ \) and \( 4.0\times10^{-10} \text{ cm}^3\text{s}^{-1} \) for the singlets. Now, we have measured a characteristic energy equal to 650 J/l for 500 ppm of ethene diluted in nitrogen, instead of 160 J/l for the same concentration of formaldehyde. Thus, assuming that quenching reactions of the nitrogen excited states are the dominant processes for the removal of these two molecules, it appears that \( k_{R4} \) and \( k_{R3} \) for formaldehyde should be higher than the corresponding coefficient values known for ethene. This is contradictory with the value of \( k_{R4} \) given by Suzuki et al. [29]. However such a discussion of experimental results obtained for the DBD-reactor remains rather qualitative without a complete physical and chemical modeling of the filamentary discharge. A more quantitative interpretation can be achieved for the homogeneous plasma of a photo-triggered reactor.

B. Results for homogeneous plasma and kinetic interpretation

In our modeling, we take into account all possible dissociation reactions of CH$_2$O, and reactions of by-products. Ionization of the molecule by electron impact is known [31], but there is very few data on cross sections for the production of electronic excited states [32]. Therefore, we have taken the well-known data for methane [33] about processes leading to neutral products (H, H$_2$, CO, HCO) [28], with an offset for the threshold energy [30]. The major product ions are: CH$_2$O$^+$, HCO$^+$, and CO$^+$ [31].

The figure 3 presents the concentration of formaldehyde measured at the exit of the UV2412 reactor, for an initial concentration equal to 300 ppm diluted in nitrogen. Experimental results are compared to predictions of the self-consistent model (lines) considering different dissociation kinetics for CH$_2$O.

Dashed lines denoted 1a and 1b correspond to the kinetic taking into account the reaction (R4a) together with (R4b) (with 50 % branching ratios), or (R4b) together with (R4c) (idem) respectively. Using of these two different dissociation kinetics allows evaluating the effect of the hydrogen atom production on the CH$_2$O removal, see reaction (R8). In both cases 1a and 1b, the overall reaction coefficient given by Suzuki et al. [29] is used, and we assume reaction (R12) for the singlet states with a much higher coefficient value according to the literature about other compounds [7, 10, 30], \( k_{R12}=5.0\times10^{-10} \text{ cm}^3\text{s}^{-1} \). It can be seen that model predictions overestimate the formaldehyde concentration as compared to the measurement results. The importance of the chosen dissociation kinetic is very low. Moreover, we have established that an increase of the singlet states quenching coefficient by one order of magnitude does not improve very much the results, showing that the major role for the decomposition of the formaldehyde molecule is played by the \( \Lambda^\Sigma_u^+ \) state in our experimental conditions. Full lines denoted 2a and 2b corresponds to predictions for an overall coefficient \( k_{R4}=5.0\times10^{-10} \text{ cm}^3\text{s}^{-1} \), all things being equal. In this case there is a much better agreement with the experiment. Finally, the following by-products are suggested: H+HCO (50 %), and H$_2$+CO (25 %), and H+H+CO (25 %), giving the best agreement with all experimental points; this agreement is emphasized in figure 5 (line marked by: N$_2$).

Carbon oxide is an interesting species for the validation of the proposed kinetic scheme. In figure 4 is plotted its concentration for same conditions than in figure 3. Predictions for cases 2a and 2b are closed to measurement results, the best agreement being obtained for 2a: the dissociation products from (R4)-type reactions are identical to those issued from UV-photodissociation processes [32].
Results in this figure also confirm that the kinetic schemes with \( k_{R4} \) from Suzuki et al. [29] are unable to explain the measured CO concentration values, in consistency with results about formaldehyde.

As for the DBD-reactor, the formaldehyde removal efficiency decreases as soon as some oxygen is added to the mixture. Therefore, the kinetics involved in the two types of discharges looks very similar. The figure 5 presents the concentration of formaldehyde measured at the exit of the UV2412 reactor, for an initial concentration equal to 300 ppm diluted in nitrogen or in a mixture containing 3 % of oxygen. Measurements are compared to predictions of the self-consistent model.

![Fig. 5. Concentration of formaldehyde at the exit of the UV2412 reactor, for 300 ppm diluted in N2 or N2/O2 (3 %) at 400 mbars. Lines are predictions of the self-consistent 0D model.](image)

The full lines correspond to predictions for \( k_{R4}=5.0 \times 10^{-10} \, \text{cm}^3\text{s}^{-1} \), and by-products: \( \text{H}^+\text{HCO} \) (50 %), and \( \text{H}_2^+\text{CO} \) (25 %), and \( \text{H}^+\text{H}^+\text{CO} \) (25 %). For the mixture with oxygen, the dashed line is for the value of \( k_{R4} \) given by Suzuki et al. [29]. A good agreement is obtained between predictions and measurement results for both mixtures studied, and the computation results using \( k_{R4}=4.7 \times 10^{-12} \, \text{cm}^3\text{s}^{-1} \) is not so far from experimental points. However, in this case, the formaldehyde concentration at the exit of the reactor decreases at a fixed number of current pulses when oxygen is added to \( \text{N}_2\text{CH}_2\text{O} \); this is not consistent with the measurement results.

V. ACETALDEHYDE REMOVAL

As for formaldehyde, the removal of acetaldehyde diluted in mixtures of atmospheric gases involves dissociation processes by collisions with the nitrogen excited states [13-15, 34]. Very few data exist about such processes. Recently we proposed the following scheme deduced from experimental and modeling studies on the UV-510 reactor [15], for main dissociation mechanisms,

\[
\begin{align*}
\text{N}_2(A^3\Sigma^+ u) + \text{CH}_3\text{CHO} & \rightarrow \text{CH}_3 + \text{HCO} + \text{N}_2 \quad \text{(R16a)} \\
\text{N}_2(A^3\Sigma^+ u) + \text{CH}_3\text{CHO} & \rightarrow \text{CH}_4 + \text{CO} + \text{N}_2 \quad \text{(R16b)} \\
\text{N}_2(A^3\Sigma^+ u) + \text{CH}_3\text{CHO} & \rightarrow \text{CH}_2\text{CO} + \text{H}_2 + \text{N}_2 \quad \text{(R16c)}
\end{align*}
\]

with an overall coefficient \( k_{R16}=5.5 \times 10^{-11} \, \text{cm}^3\text{s}^{-1} \). These reactions are compatible with bond energies in the acetaldehyde molecule [25]; the minimum is for \( \text{C}-\text{C} \), 2.92 eV. Also, the energy of the first triplet electronic excited states of \( \text{CH}_3\text{CHO} \) is closed to the energy of \( \text{N}_2(A^3\Sigma^+ u) \) [35]. Moreover CO, methane, and hydrogen were identified as major by-products both in homogeneous and filamentary nitrogen plasmas [14, 15], strengthening the dissociative channels proposed above. As for \( \text{CH}_2\text{O} \), the carbon monoxide also comes from the reactions (R6) and (R7), and from,

\[
\text{CH}_3 + \text{HCO} \rightarrow \text{CH}_4 + \text{CO} \quad \text{(R17)}
\]

Several other reactions can be invoked for the production of \( \text{H}_2 \) and \( \text{CH}_4 \) reaction (R5) and (R15), and,

\[
\begin{align*}
\text{H} + \text{CH}_3\text{CHO} & \rightarrow \text{H}_2 + \text{CH}_3\text{CO} \quad \text{(R18)} \\
\text{H} + \text{CH}_3\text{CO} & \rightarrow \text{CH}_2\text{CO} + \text{H}_2 \quad \text{(R19)}
\end{align*}
\]

The recombination reaction,

\[
\text{HCO} + \text{CH}_3 \rightarrow \text{CH}_3\text{CHO} \quad \text{(R20)}
\]

limits the acetaldehyde removal, but it is not enough efficient to hinder the effect of \( \text{N}_2 \) states quenchings, reactions (R16a-c).

Similarly to \( \text{CH}_2\text{O} \), we have developed a kinetic scheme for the acetaldehyde diluted in \( \text{N}_2\text{O}_2 \) [15], taking into account all processes involved such as dissociations of the pollutant molecule (electron collisions, \( \text{N}_2 \) states quenching), many reactions concerning the by-products, and oxidation reactions (see part VI).

![Fig. 6. Concentration of acetaldehyde after the discharge in the UV510 reactor, for 5000 ppm diluted in N2 or N2/O2 at 460 mbars. Line : predictions of the self-consistent 0D model.](image)

In figure 6 is plotted, for an initial concentration of 5000 ppm, the acetaldehyde concentration (normalized with respect to \( \text{C}_0 \)) removed in the discharge volume of the UV510 reactor, following one current pulse excitation (see part II), as a function of the oxygen percentage in the \( \text{N}_2\text{O}_2/\text{CH}_3\text{CHO} \) mixture. The full line corresponds to the model predictions. The increase of the converted \( \text{CH}_3\text{CHO} \) concentration, \( \text{C}_{\text{conv}} \), when the
oxygen concentration increases, is well described by the model.

VI. ABOUT THE EFFECT OF OXYGEN

In the N$_2$/O$_2$/CH$_2$O mixture, the formaldehyde is oxidized by the oxygen atom

\[ \text{O}(^3\text{P}) + \text{CH}_2\text{O} \rightarrow \text{HCO} + \text{OH} \] \hspace{1cm} (R21)

followed by,

\[ \text{OH} + \text{CH}_2\text{O} \rightarrow \text{HCO} + \text{H}_2\text{O} \] \hspace{1cm} (R22)

In the reaction (R21), O($^3\text{P}$) is produced by dissociation processes of the oxygen molecule, including,

\[ \text{N}_2(A^3\Sigma_u^+) + \text{O}_2 \rightarrow \text{O}(^3\text{P}) + \text{O}(^3\text{P}) + \text{N}_2 \] \hspace{1cm} (R23)

Note that the hydroxyl radical is much more reactive with CH$_2$O than the oxygen atom at low temperature, the respective coefficients for (R21) and (R22) being: $k_{R21} = 1.7 \times 10^{-13}$ cm$^3$s$^{-1}$ and $k_{R22} = 1.0 \times 10^{-11}$ cm$^3$s$^{-1}$, at 300 K [19, 20]. This radical is also formed by the efficient three body recombination reaction [9],

\[ \text{H} + \text{O}(^3\text{P}) + \text{N}_2 \rightarrow \text{OH} + \text{N}_2 \] \hspace{1cm} (R24)

However the production of OH in the dry mixture and the oxidation reactions of CH$_2$O are not efficient enough; (R21) and (R22) cannot compensate the decrease of the rates for (R4a-c) when oxygen is added to N$_2$/CH$_2$O, owing to the loss of nitrogen metastable states by (R23). Therefore, as shown in figure 5, the formaldehyde concentration at the exit of the photo-triggered reactor is higher for the mixture containing oxygen than for N$_2$/CH$_2$O, all things being equal. For conditions of this figure, and for one current pulse, the reactions (R21) and (R22) participate respectively for 3.0 and 31.8 % to the removal of CH$_2$O, while quenching of N$_2(A^3\Sigma_u)$ participate for 21.7 %, and quenching of the singlet states for 2.1 %.

Unlike to formaldehyde, for [O$_2$] lower or equal to 5 %, the rapid increase of the converted concentration of the acetaldehyde in the N$_2$/O$_2$/CH$_3$CHO mixture (figure 6) is clearly the effect of the more and more higher importance of the oxidation reactions, namely:

\[ \text{O}(^3\text{P}) + \text{CH}_3\text{CHO} \rightarrow \text{CH}_2\text{CO} + \text{OH} \] \hspace{1cm} (R25)

\[ \text{OH} + \text{CH}_3\text{CHO} \rightarrow \text{CH}_2\text{CO} + \text{H}_2\text{O} \] \hspace{1cm} (R26)

At 300 K: $k_{R25} = 4.7 \times 10^{-13}$ cm$^3$s$^{-1}$ and $k_{R26} = 1.6 \times 10^{-11}$ cm$^3$s$^{-1}$ [19, 20]. The relative importance of these two reactions roughly corresponds to what is observed for formaldehyde. However, the corresponding coefficients are higher than those for CH$_2$O, whereas it is the contrary for dissociation reactions. For acetaldehyde, the role of the dissociative reactions (R16a-c) decreases owing to (R23) but the oxidation of CH$_3$CHO compensates for this decrease.

For photo-triggered reactors, the influence of the oxygen percentage on the removal of the aldehyde molecules was not studied experimentally for a large range of initial concentration values; for CH$_2$O, C$_0$ was equal or less than 300 ppm (UV2412 reactor), and for CH$_3$CHO, it was higher than 1000 ppm (UV510). However model predictions show that, at 300 ppm of acetaldehyde, the concentration removed in the discharge does not depend upon the oxygen percentage (from 1 % up to 20 %), i.e. the increase of the oxygen content does not induce a decrease of the removal efficiency of CH$_3$CHO. Moreover, the efficiency is lower for the N$_2$/CH$_3$CHO mixture (73 %) than for the mixture with 1 % of added oxygen (89 %). Thus, even if the concentration is low, this behavior remains different to what was established for the formaldehyde.

VII. CONCLUSION

The dissociation of some VOCs due to collisional quenching of the nitrogen metastable excited states can play a non-negligible role in the conversion of such pollutants diluted in N$_2$/O$_2$ mixtures. At low temperature, the oxidation reactions by the oxygen atom or by the hydroxyl radical are not always sufficiently effective to induce an increase of the pollutant removal when oxygen is added to the N$_2$/VOC mixture. A general rule can be hardly established because it depends on the molecule. A knowledge as accurate as possible of the quenching coefficients is necessary. Experimental and modeling studies on the conversion of formaldehyde and acetaldehyde in homogeneous nitrogen plasmas emphasize that the quenching coefficient of N$_2(A^3\Sigma_u)$ by CH$_2$O should be higher than the one for the quenching by CH$_3$CHO, by about one order of magnitude.

In addition to the VOC molecule, the measurements of other species (for example ozone) concentrations in the photo-triggered reactors might be useful for a more complete validation of the kinetic model proposed and discussed in the present work. It opens the way for further studies.

References


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