

Dissociation against oxidation kinetics for the conversion of VOCs in non-thermal plasmas of atmospheric gases^{*}

Stéphane Pasquiers^a, Nicole Blin-Simiand, and Lionel Magne

Laboratoire de Physique des Gaz et des Plasmas, Université Paris-Sud, CNRS, Université Paris-Saclay, 91045 Orsay cedex, France

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Abstract. The kinetics of four volatile organic compounds (VOCs) (propene, propane, acetaldehyde, acetone) were studied in plasmas of atmospheric gases using a photo-triggered discharge (homogeneous plasma) or a dielectric barrier discharge (filamentary plasma). It was shown for the homogeneous plasma that quenchings of nitrogen metastable states, $A^3\Sigma_u^+$ and the group of singlets $a' \ ^1\Sigma_u^-$, $a \ ^1\Pi_g$ and $w \ ^1\Delta_u$, are important processes for the decomposition of such molecules. Recent measurements of the H_2 concentration produced in the N_2/C_3H_6 mixture emphasize that the hydrogen molecule can be an exit route for propene dissociation. It is also found that H_2 and CO molecules are efficiently produced following the dissociation of CH_3COCH_3 and the subsequent chemical reactivity induced by radicals coming from acetone. Addition of oxygen to a N_2/VOC mixture can change drastically the kinetics. However, the quenching processes of N_2 metastables by the VOC are always present and compete with oxidation reactions for the conversion of the pollutant. At low temperature, oxidations by O or by OH are not always sufficiently effective to induce an increase of the molecule decomposition when oxygen is added to the mixture. In particular, the presence of O_2 has a detrimental effect on the acetone removal. Also, as evidenced for acetaldehyde and propane, some kinetic analogies appear between filamentary and homogeneous plasmas.

1 Introduction

Non-thermal plasmas in mixtures of atmospheric gases (N_2 , O_2 and H_2O) have been widely studied, in particular owing to their use in the conversion of VOCs emitted by human activities [1–12]. These plasmas are often produced by pulsed discharges (corona, dielectric barrier, pre-ionised...) of short duration (<100 ns), wherein a complex molecular kinetics takes place. Discharges can be coupled to catalysis in order to achieve the best energy efficiency for the total oxidation of the pollutants [6–12]. However a comprehensive description of the VOCs decomposition kinetics in the plasma phase is always needed for the process optimization. Indeed, many compounds should be produced owing to the decomposition of the primary pollutant, which must be further oxidized by adequate catalysts.

Species involved in the conversion of a VOC can be either the oxygen atom or the hydroxyl radical, but also the nitrogen metastable states which are an important energy reservoir. The exact role of these states must be determined, because quenching collisions should lead to

the dissociation of the colliding partner through electronic excitation transfer [13]. In this paper, we discuss the kinetics of some compounds belonging to the hydrocarbons, aldehydes and ketones families chosen as examples to get insight into the decomposition mechanisms of organic molecules. Studies for homogeneous plasma of a pre-ionized (photo-triggered) discharge [14] are presented and the importance of quenching collisions of the nitrogen metastable states is highlighted. The conversion of molecules in a dielectric barrier discharge (DBD) [15] is also studied.

Previously published studies for the homogeneous plasma and for different molecules (propene, propane and acetaldehyde) are recalled and compared for discussion purposes of new results obtained on propene (experimental and theoretical) and acetone (experimental). Furthermore, kinetic analogies between highly filamentary (DBD) and homogeneous discharges are discussed for the first time for propene, propane and acetaldehyde.

2 Experiments and modeling

2.1 Studies for homogenous plasmas

Homogeneous cold plasmas can be obtained at sub-atmospheric pressure in different gas mixtures containing

^a e-mail: stephane.pasquiers@u-psud.fr

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N_2 , O_2 , H_2O , by using a photo-triggered discharge [14]. The physics of such a discharge is known and the use of a self-consistent modeling, facing measurement results, allows studying complex plasma kinetics without simplifying hypothesis about the electrical energy deposition in the inter-electrode space [16–22]. In the past 10 years, it was shown that N_2 metastable states ($A^3\Sigma^+_u$, with an excitation threshold at 6.17 eV, but also the group of singlets: $a' ^1\Sigma^-_u$, $a ^1\Pi_g$ and $w ^1\Delta_u$, with a threshold at 8.4 eV) can play an important role in the degradation of some organic molecules [17–22]. The kinetic studies are still going on with the UV510 reactor (discharge volume of 50 cm^3), described in previously published works. New results given in the present paper, as well as those recalled from the literature, concern N_2 and N_2/O_2 mixtures with addition of a VOC at a concentration value up to 5000 ppm, for a total pressure of 0.46 bar in order to ensure a perfect homogeneity of the molecular plasma pre-ionized by UV photons. A description of the model used for the kinetic interpretation of the experimental results has been also given before. It couples: (i) the solution of the Boltzmann equation for the electrons [23], (ii) the kinetic equations describing the temporal evolution of the various species (molecular excited states, ions, atoms, radicals, molecules) produced by the discharge and during the afterglow, (iii) the electric circuit equations given by the Kirchhoff laws. As many reaction rates are sensitive functions of the gas mixture temperature, the time evolution of the temperature is also taken into account through the resolution of the energy conservation equation.

2.2 Studies for non-homogenous plasmas

Most of nanosecond pulsed discharges (corona, DBDs) in N_2/O_2 at atmospheric pressure are strongly filamentary owing to the propagation of streamers. A comprehensive kinetic interpretation of measurements in such plasmas is quite difficult because it requires a self-consistent modeling of both the streamer physics and the strongly reactive chemistry of the gas mixture. This issue becomes notably very difficult when a VOC is added in the mixture.

In addition to works using the photo-triggered discharge, we have studied the conversion of organic molecules in a DBD, rod-cylinder type, driven by a high voltage pulse. A description of the experiment can be found in reference [24]. Studied gas mixtures are composed of either N_2 or N_2/O_2 (oxygen percentage value up to 20%) at 1 bar with addition of 500 ppm of a given VOC. Such DBD plasma is very inhomogeneous; it is a very complex medium and constitutes therefore a challenge for modeling. However, it may be interesting to examine how the knowledge acquired using the homogeneous plasma, in particular about the N_2 states quenching mechanisms, can help in the understanding of the overall reactivity in the filamentary plasma.

In the present work we have used a strongly simplified physical approach, in such a way that the electrical energy release during the discharge as well as time evolutions of species densities during the current pulse are

not computed. The electron density and the reduced electric field E/N (N : total density) in the discharge volume are taken as input parameters. The electron energy transfers to the gas mixture are approximated by a spatially averaged excitation and dissociation of the initial mixture components (N_2 , O_2) in the whole discharge volume V_d . The coefficients of electronic inelastic processes are calculated solving the Boltzmann equation for the electron energy distribution function (EEDF) for an assumed value of the reduced field E/N . Note that, considering the low value of the inlet pollutant concentration, 500 ppm, the EEDF should not depend upon this molecule and it is entirely controlled by the relative amount of nitrogen and oxygen at a fixed E/N value. The density of metastable states $N_2(A^3\Sigma^+_u)$ and $N_2(a' ^1\Sigma^-_u, a ^1\Pi_g$ and $w ^1\Delta_u)$, radiative states $N_2(C ^3\Pi_u)$ and $N_2(B' ^3\Sigma^-_u)$, and atoms N as well as $O(^3P)$ and $O(^1D)$ are then calculated by multiplying these coefficients by a second parameter $Ne \times \Delta t$, corresponding to an assumed product of the averaged electrons density in the volume V_d by the discharge duration (about 100 ns). The so obtained densities of excited states and atoms are then used as initial conditions to solve the balance equations of the heavy species during the afterglow. This equations system is solved during the time between the considered HV-pulse and the following one, i.e., during the time F^{-1} where F is the pulse repetition frequency. Finally, the gas mixture at the DBD exit has undergone $N_p = F \times V_d/Q$ successive pulses, where Q is the gas volumetric flow rate. The modification of the mixture composition during these N_p successive pulses is calculated by injecting the computed densities at the end of post-discharge $\#n$ as initial mixture composition for the pulse $\#n + 1$.

This simplified model being not self-consistent, the inputs E/N and $Ne \times \Delta t$ must be determined by comparing computation results with concentrations of molecules measured at the reactor exit. For a given flow rate, theoretical concentration of the pollutant, but also those of its main by-products, should correspond to the measured ones for each F value. Moreover, the complex kinetic schemes taken into account should have been previously validated from studies on homogeneous plasma, i.e., on the photo-triggered discharge. This is particularly important for quenching processes of N_2 metastable states by VOCs, which could lead to various dissociation products, radicals or molecules, and for which very few data exist in the literature. However, contrary to the photo-triggered discharge we do not consider the kinetics of charged particles, i.e., electrons (its average density follows from the value of the input $Ne \times \Delta t$) and the various positive and negative ions produced. Here the main reason for neglecting the influence of the VOCs on the kinetics of charged particles is that the initial concentration is rather low. Moreover it has been shown that, for the homogeneous plasma, the role of charged particles on the removal of some pollutant molecules (propane [18], acetaldehyde [19]) is weak as compared to influence of N_2 metastable states, even for a high concentration of 5000 ppm.

Also, the increase of the gas temperature, T , owing to electrical energy input in the mixture is not taken into

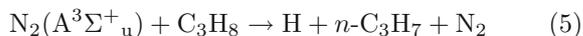
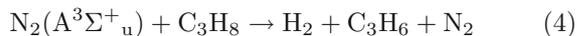
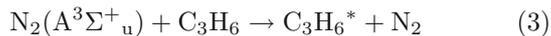
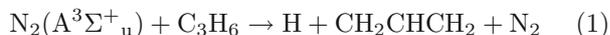
account. This simplification does not interfere the comparison between experimental and theoretical results for low specific energy values, E_S , let say less than 100 J/L; $E_S = F E_{\text{pulse}}/Q$ where E_{pulse} is the energy deposited in the discharge for each HV-pulse. A rough estimate of the maximum temperature increase, ΔT , can be made assuming no thermal loss and total conversion of electrical energy into thermal energy. At constant pressure and for 20% O₂ (or for pure N₂), it gives $\Delta T = 80$ °C (85 °C) for $E_S = 100$ J/L and $\Delta T = 750$ °C (775 °C) for $E_S = 900$ J/L, i.e., the maximum energy value in our experiment (see for example Fig. 3). This ΔT value is high for 900 J/L, but of course the real gas temperature increase should be lower owing to losses by diffusion and radiation. We have not tried to precisely determine the real ΔT value in our DBD reactor but we have established that, for mixtures containing oxygen, the ozone concentration measured at the exit of the reactor decreases with time owing to the mixture heating by the discharge [24]. This does not occur at low frequency, i.e., low E_S , emphasizing a negligible heating effect in that case. However it is clear that predictions of the model should be treated with caution when E_S is of several hundreds of J/L. Of course the maximum energy value for which the model remains valid without considering the increase of T should depend upon the considered molecule, because of different temperature dependencies of reaction coefficients included in the kinetic schemes. Anyway the most restrictive assumption remains that the plasma is considered as homogeneous, even if the temperature growth is not taken into account.

All the studies discussed in the following were carried out at an initial temperature of the gas mixture at the ambient (20 °C).

3 Results and discussion

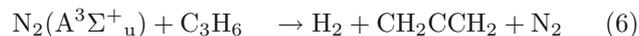
3.1 Conversion of VOCs in nitrogen plasmas

It has been previously shown [18,21] that, for the photo-triggered discharge, the removal of propane and propene molecules diluted in N₂ can be explained in great part by quenched metastables, as follows,



and same reactions for the singlets $a' \ ^1\Sigma^-_{\text{u}}$, $a \ ^1\Pi_{\text{g}}$ and $w \ ^1\Delta_{\text{u}}$, further denoted N₂(a'), and where C₃H₆* is a radiative excited state (not dissociative quenching). Branching ratios are, for propene: 27.5% both for (1) and (2),

55% for (3) and for propane: 65% (4) and 35% (5); coefficient values are given in Table 1. Kinetics of these two hydrocarbons are strongly coupled: C₃H₆ is a direct product coming from the dissociation of C₃H₈, reaction (4), and propene is also an important quencher for N₂ states with a reaction coefficient for the most populated one, N₂(A³Σ⁺_u), that is more than two orders of magnitude higher than for propane [13]. However, uncertainties remained about the exit routes for the dissociation processes of propene. Recent measurements of the H₂ concentration produced in the N₂/C₃H₆ mixture give some answers to this issue. In Figure 1 is plotted this concentration for two different charging voltage values, V_C , of the capacitor bank connected to the discharge structure. Changing V_C leads to change the energy released in the discharge, for each current pulse, from 50 J/L ($V_C = 17$ kV) up to 76 J/L ($V_C = 21$ kV) [14,16]. Experimental points are compared to predictions of the self-consistent model for two different kinetics, either by considering reactions (1)–(3) or by using the following alternative for (2),



with the following branching ratios: 50% (1), 5% (6) and 45% (3), and with unchanged coefficients. A much better agreement is obtained using (6) instead of (2), nothing else being changed in the kinetic scheme. It emphasizes that the dissociation routes chosen for the pollutant molecule are of considerable importance to explain values of by-products concentrations.

In fact quenching collisions of the nitrogen metastable states with an organic molecule leads mostly to the dissociation of this molecule. It has been often observed for N₂(A³Σ⁺_u) and it has been measured to be the dominant channel for numerous compounds [13,30,31,33–36]. Golde et al. [25] argued there is only one mechanism for quenching, electronic to electronic energy transfer to an excited state of the collision partner, which can then decompose. Later Herron [13] discussed this process in a review, and recalled that the dissociation reaction may be dependent on the acceptor species. About hydrocarbons, Meyer et al. [31] have previously suggested that the decomposition of C₂H₄ and cis-C₄H₈ follows the creation of an electronically excited triplet state of the olefin. Also, many studies have been performed on methane [13] and the hydrogen atom has been detected as a product [25]. Apart from hydrocarbons like propene and propane [18,21], our studies using the photo-triggered discharge have brought out the dissociation of some oxygenated VOCs like acetone and iso-propanol [17].

As shown in Figure 2, our most recent measurements emphasise that H₂ and CO molecules are efficiently produced following the dissociation of CH₃COCH₃ and the subsequent chemical reactivity induced by radicals coming from acetone. Carbon monoxide and hydrogen concentrations measured in the whole volume (9 L) of the device embedding the UV510 discharge are plotted as function of the number of current pulses undergone by the gas mixture (see [18] for more detail about the experiment), up to 250, for 5000 ppm of acetone diluted in N₂ and for a

Table 1. Reactions coefficients (in $\text{cm}^3 \text{s}^{-1}$) for propene, propane, acetaldehyde and acetone, for N_2 metastable states quenchings (including all exit routes) and oxidation processes by $\text{O}(^3\text{P})$ and OH (at 25°C). Values for oxidation processes are taken from [30,32].

Molecule	$\text{N}_2(\text{A}^3\Sigma^+_{\text{u}})$	N_2 (singlets)	$\text{O}(^3\text{P})$	OH
Propene	2.8×10^{-10} [13]	2.8×10^{-10} [21]	4.8×10^{-12}	7.9×10^{-11}
Propane	1.3×10^{-12} [13]	3.0×10^{-10} [13]	1.4×10^{-14}	1.2×10^{-12}
Acetaldehyde	4.2×10^{-11} [19]	4.0×10^{-10} [19]	4.6×10^{-13}	1.6×10^{-11}
Acetone	1.1×10^{-10} [13]	unknown	7.0×10^{-16}	2.2×10^{-13}

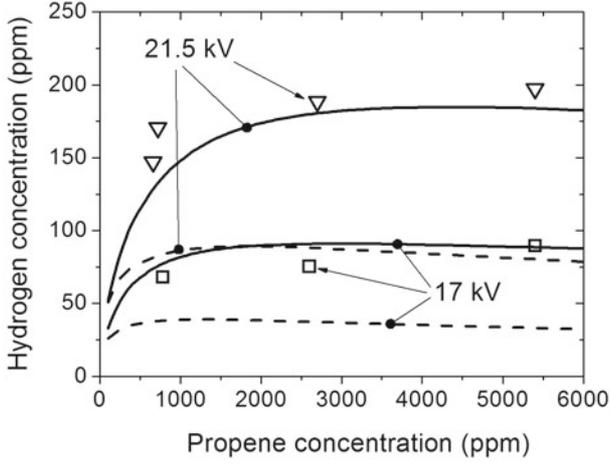
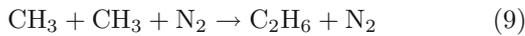
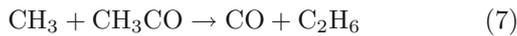


Fig. 1. Concentration of hydrogen produced in the photo-triggered discharge, for one current pulse, and for two different values of the capacitors charging voltage. Lines are predictions of the self-consistent model, for two different kinetic schemes, see text for details.

deposited energy equal to 4.6 J at each pulse ($V_C = 23 \text{ kV}$, specific energy equal to 92 J/L); the converted acetone is also given on the diagram. A high amount of CO is produced. Both H_2 and CO concentrations increase linearly when the number of current pulses increases, and the carbon monoxide one is approximately twice the hydrogen one. Also shown in Figure 2, methane and ethane are coming from the conversion of acetone; the concentration of CH_4 being equal to the concentration of H_2 and the concentration of C_2H_6 being half thereof. All these experimental results suggest that H, CH_3 and CH_3CO are produced by acetone dissociation. CO, CH_4 and C_2H_6 should come more probably from the reactivity or recombination of these radicals, i.e.,



However such a conclusion is not obvious for H_2 when one examines the existing literature about quenching of N_2 states by hydrocarbons or VOCs. For example, a molecular elimination process has been demonstrated by

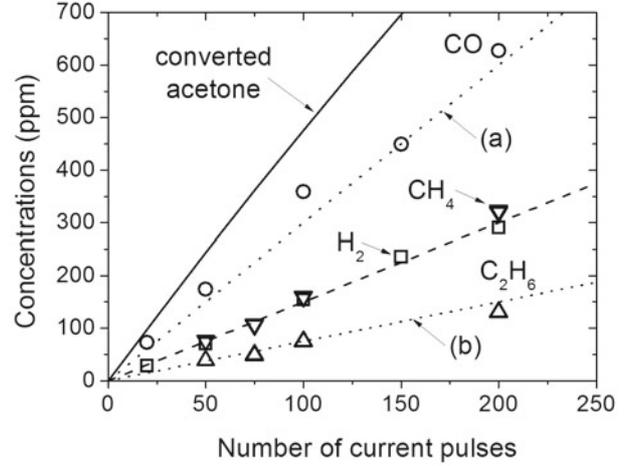
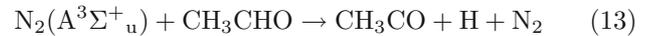
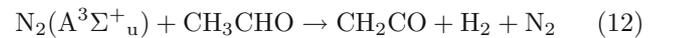
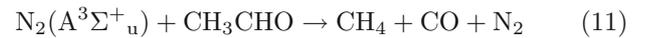
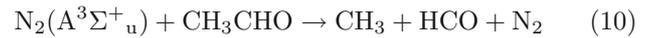


Fig. 2. Concentration of some by-products (CO, H_2 , CH_4 , C_2H_6), together with the converted acetone, in the device embedding the UV510 discharge, for 5000 ppm of acetone diluted in N_2 and for a deposited energy equal to 4.6 J at each pulse. Dashed line: best fit of the hydrogen concentration. Dotted lines (a) and (b) are for the hydrogen concentration multiplied by 2 and 0.5 respectively.

Umemoto [26] showing that H and H_2 are both produced following the collision of $\text{N}_2(\text{A}^3\Sigma^+_{\text{u}})$ with ethene. In addition, this question remains also open for the production of CH_4 if one takes into consideration studies about another saturated VOC, acetaldehyde [19]. Modeling of the homogeneous plasma reactivity for the $\text{N}_2/\text{CH}_3\text{COCH}_3$ mixture is underway to get a clearer interpretation of experimental results presented in Figure 2.

As mentioned above, studies have been also performed for acetaldehyde using the photo-triggered discharge [19], leading to the following proposals for quenching of the triplet state,



with the following branching ratios: 45% (10), 30% (11), 17% (12) and 8% (13). Same reactions occur for the singlets, $\text{N}_2(\text{a}')$, but with 31.5% (equivalent to 10), 21% (11),

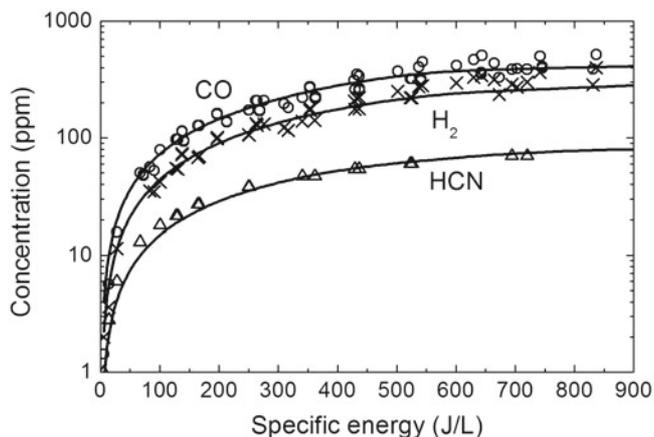
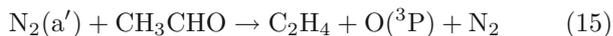
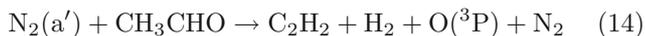


Fig. 3. Concentrations of CO, H₂ and HCN at the exit of the DBD. Initial concentration of acetaldehyde in N₂: 500 ppm. Lines: results of the simplified model.

12% (12) and 5.5% (13), and two reactions inducing breaking of the double bond C=O,



with a branching ratio of 15% for each. This kinetic scheme has already been used in a tentative interpretation of measurements performed on the pulsed DBD [27]. Figure 3 presents the experimental and predicted concentrations of the predominant products CO, H₂ and HCN at the reactor exit, for the N₂/CH₃CHO mixture. Concentrations are given as function of the specific energy E_S . For these computations, $E/N = 200$ Td and $\text{Ne} \times \Delta t = 1.1 \times 10^3 \text{ cm}^{-3} \text{ s}$; such values allows to reproduce the decrease of the acetaldehyde concentration when E_S is increased. Figure 3 shows that the previously validated kinetic scheme obtained from studies on homogeneous plasma can be usefully applied to the non homogeneous one. Kinetics seems analogous for the two types of discharges. Although the model is very simplified with respect to actual physical and chemical phenomena occurring in the filamentary plasma, it allows predicting correctly the main types of by-products in correct order for their concentration (CO > H₂ > HCN); methane is also present in the gas flow exiting the DBD, with a concentration very close to the carbon monoxide one. Moreover, model predictions are in agreement with experimental results at low but also at high energy values, showing that the increase of the gas temperature for E_S equal to several hundreds of J/L seems to have little influence. In summary it appears that the filamentary nature of the DBD does not interfere kinetic interpretations in case of the acetaldehyde diluted in N₂, at least for the most populated by-products.

Because of the chosen simplified approach, there is not unique values for the input parameters E/N and $\text{Ne} \times \Delta t$ allowing to reproduce the decrease of the concentration of the pollutant molecule, acetaldehyde for example, when the HV-pulse frequency is increased. However, the

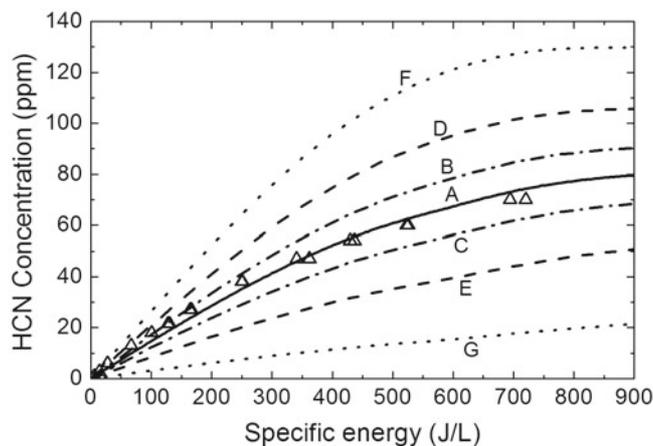


Fig. 4. Concentrations of HCN for same conditions than Figure 3. Lines are predictions of the simplified DBD reactor model for different values of input parameters E/N (in Td) and $\text{Ne} \times \Delta t$ (in $10^3 \text{ cm}^{-3} \text{ s}$): in full, (A): 200 and 1.1 – in dotted-dashed, (B): 220 and 0.9, (C): 180 and 1.4 – in dashed, (D): 250 and 0.7, (E): 150 and 2.2 – in dotted, (F): 300 and 0.5, (G): 100 and 9.1.

parameters values can have an important impact on concentrations of some main by-products. An example is given in Figure 4, showing the concentration of hydrogen cyanide produced in the N₂/CH₃CHO mixture, see also Figure 3. Lines correspond to model predictions for seven couples of E/N and $\text{Ne} \times \Delta t$ values verifying the above described criterion. For the whole range of specific energy values studied, these values cannot reasonably deviate by more than 10% for E/N and 20% for $\text{Ne} \times \Delta t$ (lines B and C in Fig. 4) with respect to the most adequate ones: 200 Td and $1.1 \times 10^3 \text{ cm}^{-3} \text{ s}$ (line A). Although in the right order of magnitude, this field value is a few higher than the one commonly accepted as the relevant volume-averaged electric field experienced by a multi-filaments nitrogen plasma, i.e., equal to the breakdown threshold, 150 Td [28]. However, it must bear in mind that it is determined for a given reactor geometry, type of dielectric material, and for a given waveform for electrical excitation. About the volume average electron density, considering that the density value in one microdischarge is at least 10^{14} cm^{-3} with a diameter of about 100 μm [15], it can be roughly estimated from the retained value for $\text{Ne} \times \Delta t$ ($\text{Ne} \approx 10^{10} \text{ cm}^{-3}$) that the number of plasma filaments created in the gas mixture is about 50. It appears consistent with previous ICCD camera measurements performed on this DBD-reactor [29].

The simplified model has been also applied to the N₂/C₃H₆ and N₂/C₃H₈ mixtures (Fig. 5). Changing the molecule should not involve changing the values of E/N and $\text{Ne} \times \Delta t$. Indeed, considering the low value of the inlet pollutant concentration, 500 ppm, the EEDF should not depend upon the type of this molecule and, as a result, production rates for nitrogen and oxygen excited states and atoms should be constant, i.e., E/N and $\text{Ne} \times \Delta t$ should be invariables. Of course this reasoning remains valid only if the non spatial homogeneity of the

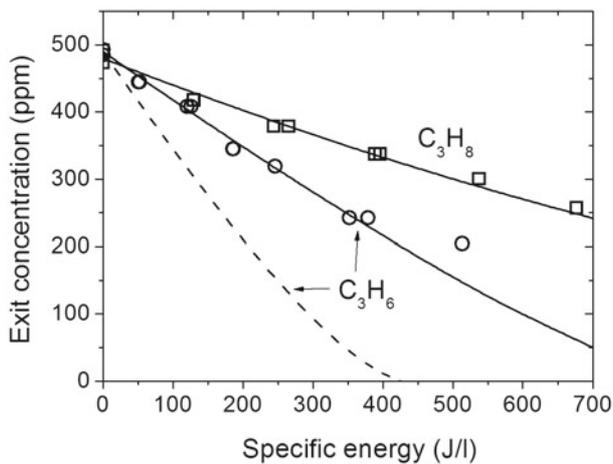
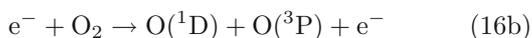
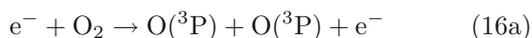


Fig. 5. Propene and propane concentrations at the exit of the DBD in N_2/C_3H_6 and N_2/C_3H_8 mixtures for an inlet hydrocarbon concentration equal to 500 ppm. Lines: results of the simplified model, see text for details.

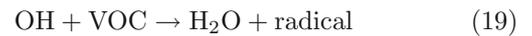
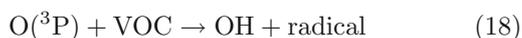
experimental discharge does not have a strong effect on the overall plasma reactivity, and thus on the exit concentration values. As shown in Figure 5 giving the exit concentration values for propene and propane (full lines), computation results are in very good accordance with experimental points for C_3H_8 , but not for C_3H_6 for which the model overestimates the removal of the molecule. For propene, the agreement between measurements and predictions is obtained for $Ne \times \Delta t$ about a factor of 2 below the value for CH_3CHO and C_3H_8 , i.e., $0.5 \times 10^3 \text{ cm}^{-3} \text{ s}$ (dashed curve in Fig. 5), but this cannot be justified for the physical reasons mentioned above. For the first value of $Ne \times \Delta t$, i.e., $1.1 \times 10^3 \text{ cm}^{-3} \text{ s}$, numerous physical and chemical explanations can be invoked for the noted disagreement. For example, recombination reactions of radicals can lead to the formation of propene, which could take a greater importance in the filamentary plasma than in the homogenous one, thus limiting the removal of the molecule.

3.2 Effect of oxygen on the conversion of VOCs

Addition of oxygen to a N_2/VOC mixture can change drastically the kinetics. Indeed, oxidation reactions take place owing to the production of O following the dissociation of O_2 by electron collisions as well as by quenching of the N_2 excited states, N_2^* , i.e.,



followed by



taking into account that the metastable state $O(^1D)$ is rapidly quenched down to the ground state and so it should only marginally participate to oxidation of the molecule (but this issue deserves to be studied more precisely for some VOCs because the coefficient for the reaction with the metastable can be several order of magnitude higher than the one for the ground state). However, the quenching processes of N_2 metastables by the VOC are always present and compete with oxidation reactions for the conversion of the pollutant. Roughly speaking, one can say that relative importance of dissociation and oxidation processes is mainly governed by: (i) the concentration of O_2 , (ii) the efficiency of the discharge to produce N_2 metastables and $O(^3P)$, (iii) values of quenching coefficients of these states by the VOC compared to quenching by O_2 , (iv) the type of radicals generated by quenching processes, playing a role on the overall kinetics of the energized gas mixture.

A self-consistent model coupling the energy deposition and the plasma kinetics appears very useful to handle this issue. It can be done for the photo-triggered discharge. Examples of results obtained for $N_2/O_2/C_3H_8$ [22] and $N_2/O_2/CH_3CHO$ [20] are displayed in Figure 6, on which are plotted the molecule concentrations removed in the discharge volume for an initial value equal to 5000 ppm, and for a specific energy equal to 92 J/L ($V_C = 23 \text{ kV}$). Measurements and predictions are in good agreement for both molecules and emphasize that the removed concentration depends weakly of the oxygen percentage. From 0 up to 20%, it increases a little bit more for CH_3CHO than for C_3H_8 . Moreover it is the highest for CH_3CHO , which is not surprising because N_2 states quenching and oxidation by $O(^3P)$ and by OH have higher coefficients for acetaldehyde than for propane, see Table 1. Although the initial mixture is dry, the hydroxyl radical can participate to the removal of the VOC because it is produced by several reactions, of course (18) but also recombination of $O(^3P)$ and H-atoms. It has been demonstrated for acetaldehyde that reaction (19) can dominate the removal, depending on the mixture composition [20].

Hydrogen, methane and ethane have been detected both for $N_2/O_2/C_3H_8$ and $N_2/O_2/CH_3CHO$. Formation of these molecules is, in part, a signature of dissociation processes producing directly H_2 (propane, acetaldehyde) and CH_4 (acetaldehyde) or methyl radicals which further recombine to form C_2H_6 (acetaldehyde).

For some molecules, the addition of O_2 to N_2/VOC can have a detrimental effect on the VOC removal. This is the case for acetone, as demonstrated in Figure 7 in which is plotted the measured removed concentration in the photo-triggered discharge (same conditions than Fig. 6). Contrary to propane and acetaldehyde, the removed concentration of acetone decreases when the oxygen percentage increases. As it can be seen in Table 1, the coefficient for N_2 states quenchings by CH_3COCH_3 is the highest for the three studied molecules, whereas the coefficients for oxidation reactions (18) and (19) for acetone are orders of magnitude lower than for the other compounds.

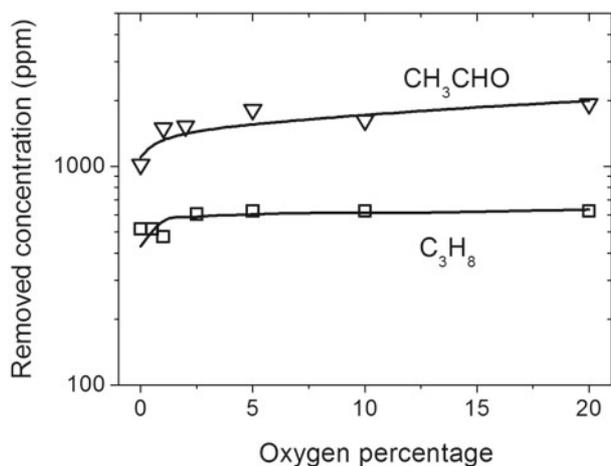


Fig. 6. Concentration of acetaldehyde [20] and propane [22] removed in the photo-triggered discharge, for one current pulse, in $N_2/O_2/CH_3CHO$ and $N_2/O_2/C_3H_8$ mixtures and for an initial concentration equal to 5000 ppm. Specific energy: 92 J/L. Lines are predictions of the self-consistent model.

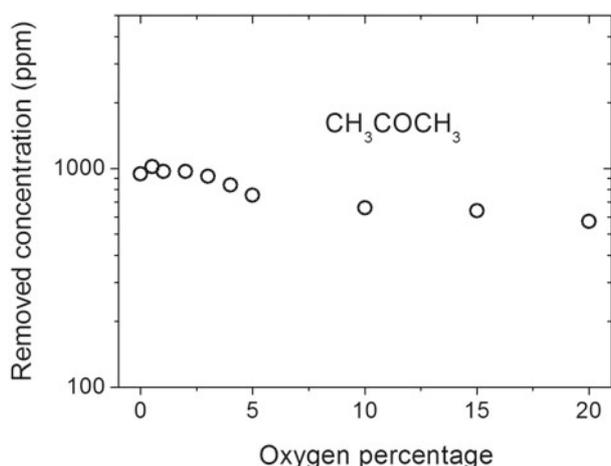


Fig. 7. Measured concentration of acetone removed in the photo-triggered discharge, for one current pulse, in the $N_2/O_2/CH_3COCH_3$ mixture and for an initial concentration equal to 5000 ppm. Specific energy: 92 J/L.

Thus, experimental results displayed in Figure 7 do not appear surprising, as compared with Figure 6.

4 Conclusion

In high pressure plasmas of N_2 and mixtures of N_2 and O_2 , quenches of nitrogen metastable states, $A^3\Sigma^+_u$ and the group of singlets $a' \ ^1\Sigma^-_u$, $a \ ^1\Pi_g$ and $w \ ^1\Delta_u$, are important processes for the decomposition of a VOC added to the mixture. It plays a fundamental role in the nitrogen plasma, but it is also present in air. 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 molecule decomposition

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.

Some kinetic analogies appear between filamentary and homogeneous plasmas, which could be very useful to get a comprehensive understanding of the physico-chemical processes in dielectric barrier or corona discharges used for the treatment of pollutants.

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