Propene and propane decomposition in atmospheric pressure nitrogen plasmas

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Propene (C_3H_6) and propane (C_3H_8) are two hydrocarbons (HC) for which the kinetics in high pressure non-thermal plasmas produced in atmospheric gases (N_2, O_2, H_2O) and their mixtures deserve to be studied. Propene is the relevant molecule for studying the treatment of automotive (diesel) combustion flue gases containing unburned hydrocarbons [1], while propane is used for researches on ignition of lean mixtures by pulsed discharges [2]. A first step in the understanding of the kinetics in the complex mixture $N_2/O_2/H_2O$/HC is the investigation of the decomposition mechanisms of the hydrocarbon molecule in the nitrogen plasma. This work presents recent results obtained by using either a photo-triggered discharge, or a dielectric barrier discharge (DBD) energized by a pulsed HV-generator.

The photo-triggered discharge produces a transient homogeneous plasma [3] at 460 mbar in a volume of 50 cm^3 for a 1 cm gap. The initial voltage between the electrodes V_0 was fixed in the 17 kV to 23 kV range. At V_0 = 23 kV, the initial reduced electric field E/N is 200 Td and the deposited energy density is E_{pp} = 92 $J.L^{-1}$ per pulse. The discharge duration is 60 ns with a current peak value of 14 kA. The DBD reactor was described in [4, 5]. The plasma is created in a Pyrex tube (Inner diameter 14.1 mm). A stainless steel tape surrounding this tube is grounded, while a high voltage pulse is applied on a central tungsten rod (2 mm diameter). The discharge volume is 22 cm^3. The mixture flow rate is 0.7 $L.mn^{-1}$ at 1 bar and the electrical deposited energy density per pulse in the DBD is E_{pp} = 2.95 $J.L^{-1}$. The total energy density deposited in the mixture can be varied changing the frequency of the discharge pulses, up to 1100 $J.L^{-1}$ for corresponding frequencies from 1 to 200 Hz. Removal of the HC molecules and concentrations of some by-products are measured by chromatography and compared to results of models for both set-up.

For the photo-triggered reactor, a fully self-consistent model coupling the discharge physics to the plasma chemistry is used to rigorously get insights on the kinetics processes involved in the HC removal. Coefficients for electron collisions are directly obtained from the solution of the Boltzmann equation, while those for reactions between heavy species have

been taken in great part from a critical review of various compilations [6,7]. A detailed description of this model, including the whole kinetic scheme and used references for nitrogen, can be found in [8].

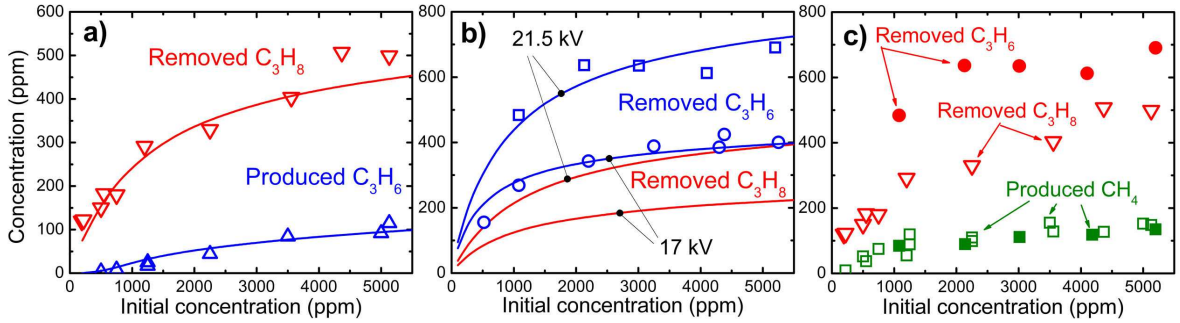

Figure 1 : comparisons between calculated and measured concentration of HC in the photo-triggered discharge for a single pulse versus the initial HC concentration. a) in a N_2-C_3H_8 mixtures at 23 kV. b) removed C_3H_6 in N_2-C_3H_6 mixtures and removed C_3H_8 in N_2-C_3H_8 mixtures. c) Removed HC and produced CH_4 full symbols in N_2-C_3H_6, hollow symbols in N_2-C_3H_8. See text for more information.

Figure 1a presents comparisons between calculated and measured concentrations of HC in the photo-triggered discharge in N_2-C_2H_8 mixtures. It can be seen that the adopted kinetic scheme gives results very close to the measurements concerning the removal of C_3H_8 and the production of C_3H_6 for a wide range of initial concentration (500-5000 ppm). Good results are also obtained on H_2 and CH_4 concentrations. It has been demonstrated in [8] that the contributions of dissociation by electron impact and ionic processes are low in front of the losses of propane by dissociation due to the quenching of nitrogen metastable states. In figure 1b, one can see that the removal of C_3H_6 in N_2-C_3H_6 mixtures is approximately twice the one of C_3H_8 in N_2-C_3H_8 for the same discharge parameters while the published value, $k_A = 2.8\times10^{-10}$ $cm^3.s^{-1}$ for the quenching coefficient of $N_2(A)$ [9] by propene is approximately two hundred times higher that for propane. Nevertheless, a satisfactory agreement between calculated removal (blue line in fig. 1b) and experiments can be obtained assuming a non-dissociative part of the quenching and the following output paths (which are unknown) for the dissociations:

$N_2(A) + C_3H_6 \rightarrow C_3H_6 + N_2$	45%	R1a
$N_2(A) + C_3H_6 \rightarrow H + CH_2CHCH_2 + N_2$	27.5%	R1b
$N_2(A) + C_3H_6 \rightarrow CH_3 + C_2H_3 + N_2$	27.5%	R1c

and considering in particular the following known recombination processes [7] :

$CH_3 + C_2H_3 \rightarrow C_3H_6$	$k=1.2\times10^{-10}$ $cm^3.s^{-1}$	R2
$H + CH_2CHCH_2 \rightarrow C_3H_6$	$k=1.4\times10^{-10}$ $cm^3.s^{-1}$	R3

It can be see in figure 1c that CH_4 concentration is similar in N_2-C_3H_6 and N_2-C_3H_8. For mixtures with propene, a high amount of methyl radical and atomic hydrogen is produced by the reaction R1c and R1b while dissociation of propane is not a source of methyl radical which is the main source of CH_4 in both mixtures by the process:

$$CH_3 + H + N_2 \rightarrow CH_4 + N_2 \quad k=1.24\times10^{-10}\ cm^3.s^{-1} \quad (460mbar, 300K) \qquad R4$$

In the case of propene, the fast recombination process R2 is a strong loss of CH_3. This could explain why CH_4 concentration is not as high as expected in N_2-C_3H_6 but similar to the one in N_2-C_3H_8.

Once the hypotheses on the kinetic of heavy particles are fixed using the studies on the photo-triggered discharge, they are tested in the modeling of the DBD reactor. The highly non-homogeneous energy deposition mechanisms are not included in the model. In this very simplified approach, the electron energy transfers to the gas mixture are approximated by an averaged excitation and dissociation of nitrogen molecules in the whole volume V_d of the discharge. The averaged densities of metastable states $N_2(A)$ and $N_2(a', a, w)$, radiative states $N_2(C)$, $N_2(B)$ and atoms N after one discharge pulse give the initial conditions to solve the balance equations of species during the time afterglow, assuming the same kinetic scheme as for the photo-triggered discharge. The gas mixture at the DBD exit has undergone N_p successive pulses, depending on the frequency of the discharge and on the residence time τ_{res} in the excitation zone. The modification of the gas mixture composition over 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 added with the supposed densities of the excited species and nitrogen atoms for one pulse.

In order to evaluate the initial density of excited species to be used as initial conditions for balance equations in the post-discharge, we defined the Γ parameter depending on E/N by :

$$\Gamma = \frac{\sum_i [N_2^*]_i + \frac{1}{2}[N]}{[N_2]}$$ so that the densities of excited species can be written as:

$$[N_2^*]_i = \Gamma \cdot [N_2] \cdot F_i \quad \text{and} \quad [N] = 2 \cdot \Gamma \cdot [N_2] \cdot F_N \quad \text{where} \quad \sum_i F_i + F_N = 1$$

For a given supposed value of E/N, F_i and F_N were fixed using a Boltzmann code in N_2. Then the values of Γ(E/N) were determined by fitting the experimental values of C_3H_8 concentration at the exit of the reactor in N_2-C_3H_8 (500 ppm). Figure 2a shows the obtained fits.

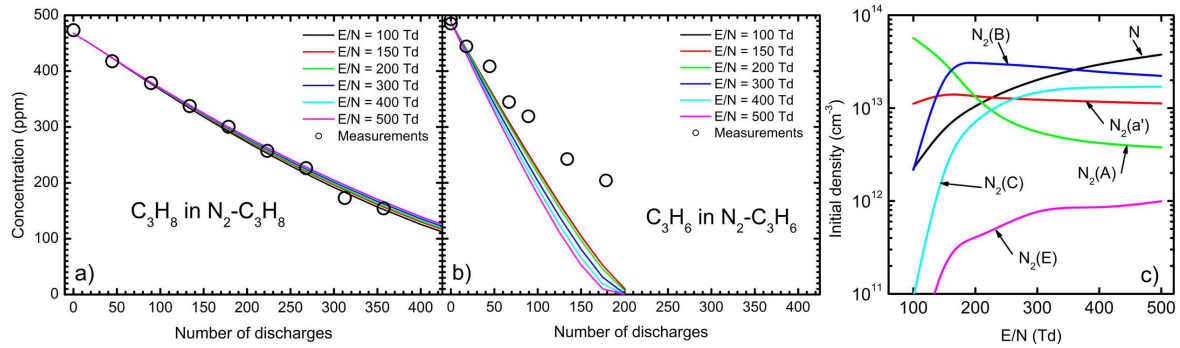

Figure 2 : comparison between calculated and measured concentration of HC at the exit of the DBD reactor versus the number of discharges in the mixture, for several hypotheses on E/N values for nitrogen excitation and dissociation. a) for C_3H_8 in N_2-C_3H_8 mixtures at 500 ppm of C_3H_8. b) for C_3H_6 in N_2-C_3H_6 mixtures at 500 ppm of C_3H_6. c) Common values, for both mixtures, of nitrogen excited states and atoms densities used as initial densities for one afterglow in the DBD (averaged values in the whole volume).

The obtained values of Γ ranges from 2.60×10^{-6} to 2.86×10^{-6}. Considering that the electrons energy distribution function is mainly determined by processes with N_2 molecules, we made the calculations in N_2-C_3H_6 with exactly the same values of Γ, F_i and F_N. The results are presented in figure 2b where it can be seen that the results of calculations are compatible with the measurements. Figure 2c shows the averaged values in the whole volume of the DBD (not in the plasma filament) of the nitrogen excited states densities used for the calculations in figure 2a and 2b.

This work is still in progress and efforts have to be made in order to better understand the kinetics of by-products in N_2-C_3H_8 and N_2-C_3H_6 mixtures in the photo-triggered discharge. Improvements of the simplified DBD model are also necessary to take into account the non-homogeneity of the plasma and its consequences on the chemistry. However, the present results seems to show that for the primary molecule kinetics (propane and propene), the scheme adopted in an homogeneous plasma produced by the photo-triggered discharge can also explain the results obtained in the strongly non-homogeneous plasma of a cylindrical DBD.

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