Production of methyl nitrate and PAN following the decomposition of acetaldehyde in atmospheric gases

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Methyl nitrate and peroxyacetyl nitrate were detected and quantified, by FTIR, at the exit of a dielectric barrier discharge used to efficiently decompose acetaldehyde diluted in N_2/O_2 mixtures. These compounds follow different kinetic paths, including dissociation of the pollutant molecule through quenchings of the nitrogen molecule metastable states. It is shown that the concentration of PAN is very sensitive to the specific energy deposited in the discharge, to the temperature, and to the operating time of the DBD until the thermal equilibrium of the reactor is reached.

The removal of acetaldehyde (CH_3CHO) in atmopsheric gas streams by non thermal plasmas has been the subject of experimental studies employing different types of pulsed electrical discharges : dielectric barrier [1, 2] or corona [3] (filamentary plasmas), as well as photo-triggered [4] discharges (homogeneous plasmas). Usually the energy efficiency of the plasma reactor is determined, and some informations about main by-products are given. At low specific deposited energy in the discharge (i.e. at low energy consomption of the de-VOC process), carbonated by-products are not completely decomposed and oxidized to give carbon oxydes. In this case a coupling of the plasma to a catalyst placed downstream should be used to complete the cleaning process. However a full description of the gas mixture composition at the exit of the discharge is required in order to use the most effective catalyst at low temperature. This study focuses on the production of nitrates issued from treatment of acetaldehyde diluted in N_2/O_2 mixtures, at 1 bar and at ambient temperaure, by a dielectric barrier discharge.

The experimental set-up is similar to the one previously used for the study of toluene [5] and formaldehyde [6] removals. The transient plasma is produced in a cylindrical DBD energised by a pulsed high voltage generator (pulse duration of about 300 ns) working at a repetition frequency value up to 200 Hz. The discharge volume is 21 cm^3. The DBD-reactor is placed in a thermo regulated oven (temperature T up to 300°C). The gas mixture introduced in this reactor, at atmospheric pressure and at a constant gas flow of 1 l/mn NTP, is composed of 500 ppm or 860 ppm of acetaldehyde in N_2/O_2 (oxygen percentage P_{O2} up to 10 %). All measurements were performed for a constant applied voltage equal to 40 kV (on a purely capacitive charge, without plasma), and the specific deposited energy was varied by changing the repetition frequency of the HV-pulse, ν. The specific energy, E_S, is simply determined by :

$$E_S = \nu E_{pulse} / F \qquad (1)$$

where E_{pulse} is the deposited energy in the plasma volume per current pulse, and F is the gas flow. This energy was determined through measurements of the voltage and the current time evolutions using adapted electrical probes connected to a fast digital oscilloscope.

Amongst other techniques, FTIR analysis was used to completely characterise the gas mixture leaving the DBD-reactor, at the outlet of the oven, in the late afterglow. The spectral resolution of the FTIR apparatus (MIR8000 spectrometer, Oriel) was 0.5 cm^{-1}. Effluents pass through a long path cell (Infrared Analysis model V-16, total volume of 2.3 L) with 12 m optical length. Methyl nitrate, CH_3ONO_2, and peroxyacetyl nitrate (PAN), $CH_3C(O)OONO_2$, were easily detected in several wavenumber areas. Their concentrations were quantified using the absorption band between 1260 and 1320 cm^{-1} [7], or 1150 and 1175 cm^{-1} [8], respectively.

In figure 1 are plotted CH_3ONO_2 and PAN concentrations as function of the specific energy for 860 ppm of acetaldehyde in the input mixure, P_{O2}=2 %, for T=20 °C and 100°C. At 20°C, both concentrations linearly increase when E_S increases up to 200 J/L (the acetaldehyde concentration decreases by 85 %); the highest growth is for methyl nitrate. However the PAN concentration saturates

at 225 J/L, and thereafter it decreases at higher energy values. The saturation effect is also found for methyl nitrate, but for 300 J/L. On the other hand, for E_S greater than 100 J/L, the PAN concentration strongly decreases when T increases up to 100°C, contrary to the methyl nitrate one which shows a weak increase at a fixed value of the deposited energy.

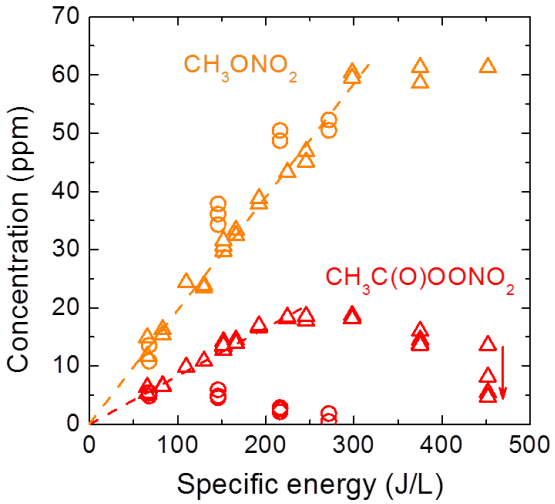

Fig. 1: Methyl nitrate and PAN concentrations at 20°C (triangles) and 100°C (circles).

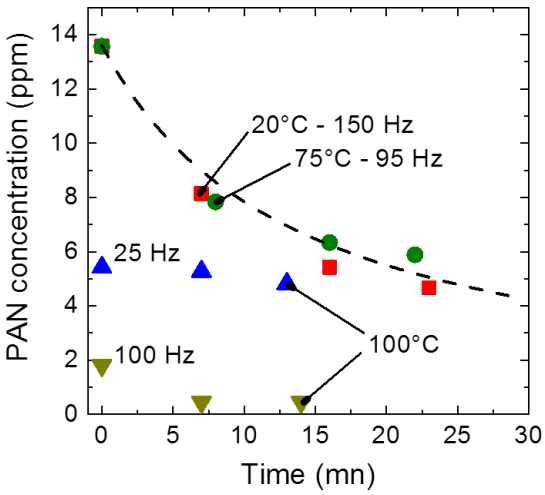

Fig. 2: PAN concentrations for different conditions of the DBD-reactor (HV-pulse frequency, oven temperature).

For different values of the high voltage pulse frequency and external warming temperature of the DBD-reactor, the figure 2 shows the PAN concentration as a function of the discharge running time. It emphasises two effects : firstly, at low temperature (20°C and 75°C), the concentration decreases during time (dashed line) for a fixed high frequency value corresponding to a high deposited energy (it can be also seen in Fig.1 for 450 J/L, arrow in the figure); secondly, it decreases at 100°C when the frequency increases, i.e. the energy increases. These effects should be related to the additional warming of the gas mixture by the discharge itself, and to the time necessary to reach the thermal equilibrium of the DBD-reactor.

The presence of CH_3ONO_2 shows that acetaldehyde is dissociated in the discharge and in the afterglow to produce CH_3,

$$\text{electron (or } N_2(A^3\Sigma^+_u)) + CH_3CHO \rightarrow CH_3 + HCO + \text{electron (or } N_2) \qquad \text{(R1)}$$

which is followed by the formation of CH_3O_2 by addition of oxygen on the methyl group, therefater the formation CH_3O through several reactions, and finally addition of NO_2 on this later radical. But two oxidation reactions also occur,

$$O(^3P) + CH_3CHO \rightarrow OH + CH_3CO \qquad \text{(R2)}$$

$$OH + CH_3CHO \rightarrow H_2O + CH_3CO \qquad \text{(R3)}$$

followed by the successive addition of O_2 and NO_2 on the CH_3CO radical to produce PAN. However this compound can readily dissociated, as confirmed by our measurements.

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