

Measurement of OH kinetics in the post-discharge of an NRP discharge

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Abstract: The post-discharge evolution of OH concentration is measured by calibrated Laser Induced Fluorescence in a nanosecond repetitively pulsed discharge. A reforming of OH in the late post-discharge, after an initial fast decay, is observed. The temporal characteristics of such reforming are monitored as a function of water concentration and the temporal sequence of discharge pulses. The results qualitatively point out the presence of a mechanism due to long-living species whose concentration might built-up in successive pulses.

Keywords: nanosecond discharges, LIF, OH kinetics

1. Introduction

In this work, we deal with a first approach to the experimental study of OH kinetics in a nanosecond repetitively pulsed discharge (NRP). The methodology is a classical LIF measurement of both the OH concentration and its time evolution in the post-discharge (or after-pulse). In addition to a general fundamental aim, this issue is relevant to the CO₂ conversion kinetics by electric discharges. Water is easily found in these discharges. It can be added to the initial mixture as a source of hydrogen, it can be present in the starting mixture such as industrial waste or biogas, or it can even be a process by-product, such as in CO₂+CH₄ dry reforming. In the presence of water, OH is easily formed in any kind of discharges, and it can contribute to the conversion kinetics, both in terms of CO₂ dissociation balance, through the back reaction:



and in terms of interesting process by-products. For example, through the reaction:



the COOH radical being an intermediate species towards the formation of carboxylic acids. The measurements presented here are taken in He-H₂O mixtures, and an attempt to add CO₂ is made in order to look at the OH kinetics in the presence of carbon dioxide. We do not try an interpretation of the observations, that require a modelling effort that is underway.

2. Experimental

The configuration of the electrodes is shown in Fig. 1. The anode is a stainless steel needle with an internal diameter of 0.7 mm. The cathode is a tungsten point shaped rod. The electrodes gap is 6 mm. The gas flows through the anode. It is kept constant at 200 sccm. The HV nanosecond-scale pulses are produced by a Megaimpulse



Fig.1 Needle-point electrode configuration

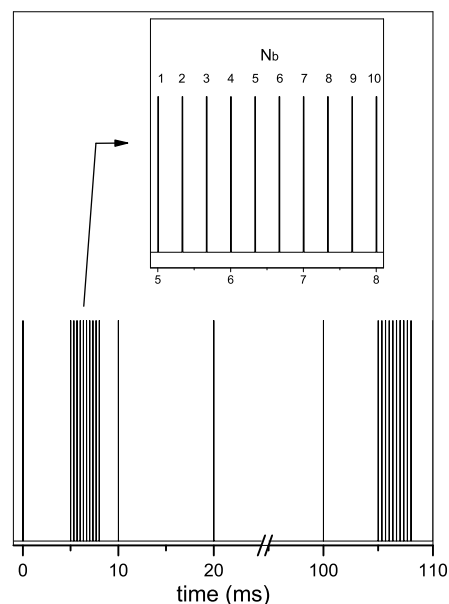


Fig. 2 The temporal pattern of discharge voltage pulses. The pattern within the bursts shown in the inset with enlarged time scale and the single pulses labelled with progressive numbers Nb.

NPG 18/3500 generator, triggered by a wave-form generator.

The pulse pattern is made of pulse bursts repeated at a frequency of 10 Hz, each burst being composed of 10 pulses at a frequency of about 2857 Hz, i.e., a burst is composed of a maximum of 10 discharge events separated by a 350 μs time interval. The pulse pattern is shown in Fig. 2. A further 100 Hz pulse pattern is superimposed in such a way that a pre-pulse always precedes by 5 ms the burst. This ensures that the first voltage pulse of the burst always produces a discharge. The number of pulses in the burst is N and can be varied up to $N_{\text{max}}=10$ equal to 10. When measuring the post-discharge after pulse N_b , the number of pulses N is set at $N=N_b$, such that post-discharge times longer than 350 μs can be explored.

3. Results

3.1. Kinetics as a function of H_2O concentration and pulses accumulation.

The decay after the first pulse ($N_b=1$) at various H_2O partial pressures is shown in Fig. 3. We observe: 1) - an initial fast decay whose rate increases on increasing H_2O partial pressure; 2) - a resurgence of $[\text{OH}]$ after about 100 μs with a maximum whose position is located at a post-discharge time T_M that decreases on increasing H_2O ; 3) - A final slow disappearance of OH. Post-Discharge behaviour depends on N_b , as shown in Fig. 4. While the initial fast decay remains almost unchanged, T_M decreases at the second pulse and remains almost the same on increasing N_b . Also, the marked dependence of T_M on H_2O concentration appears to be characteristic of the first pulse only, it being largely smoothed or even cancelled at successive pulses (see Fig. 5).

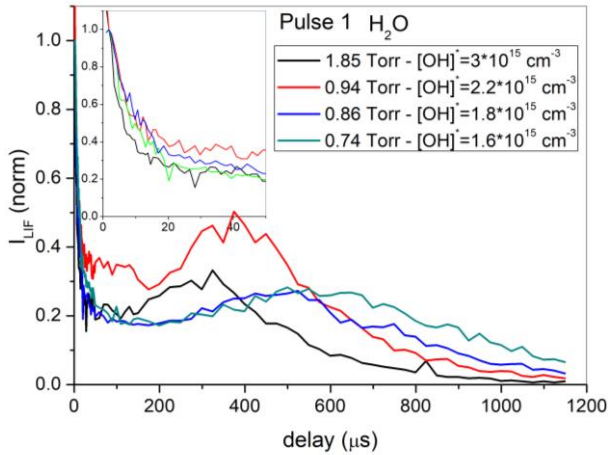


Fig. 3 $[\text{OH}]$ decay after the first pulse of the burst ($N_b=1$) for various H_2O partial pressure. The total pressure is 760 Torr. The LIF signal is normalized to the value at the post-discharge time $t_{\text{pd}} = 2\mu\text{s}$. $[\text{OH}]^*$ is the $[\text{OH}]$ absolute value at $t_{\text{pd}} = 2\mu\text{s}$.

3.2. The post-discharge kinetics is not affected by the gas flow

If the gas flow remained collimated at the needle diameter, it would cross the discharge gap in about 700 μs .

The post-discharge maximum might then be due to a flow transportation from a region with higher $[\text{OH}]$. This is not indeed the case, as reported in Fig. 6, where different flow cases are compared, and even a static gas condition is reported. Both the initial decay and T_M appear to be unaffected by the flow conditions.

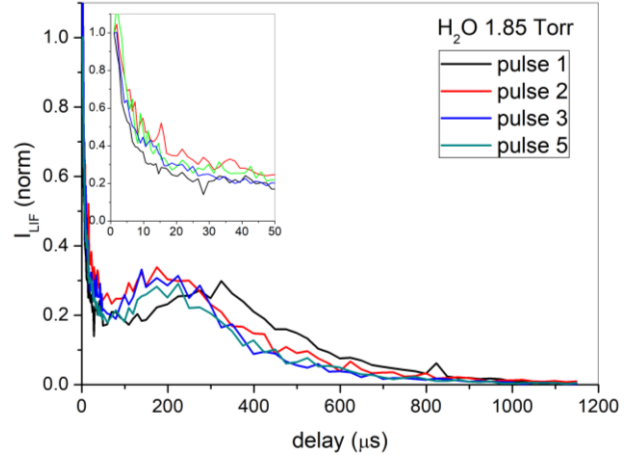


Fig. 4 $[\text{OH}]$ decay after successive pulses of the burst. The LIF signal is normalized to the value at the post-discharge time $t_{\text{pd}} = 2\mu\text{s}$.

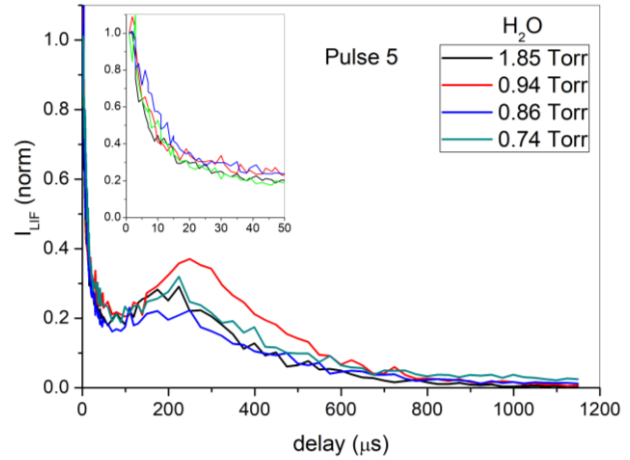


Fig. 5 $[\text{OH}]$ decay after the fifth pulse of the burst ($N_b=5$) for various H_2O partial pressure. The total pressure is 760 Torr. The LIF signal is normalized to the value at the post-discharge time $t_{\text{pd}} = 2\mu\text{s}$.

3.3. OH post-discharge kinetics on addition of CO_2

The addition of CO_2 causes an increase in the initial decay rate and a decrease in the OH concentration. On the contrary, T_M remains unchanged. This is shown in Fig. 7.

4. Discussion

The initial decay of OH concentration depends on both water content and discharge pulse in the burst. It becomes faster on increasing water, at any pulse (N_b), while it slows down on increasing N_b at fixed water content. The same happens with CO_2 addition. It is also very interesting to

point out that the OH reforming in the late afterglow is faster on addition of water and on increasing N_b . This reforming is then clearly attributable to long-living species formed in the discharge.

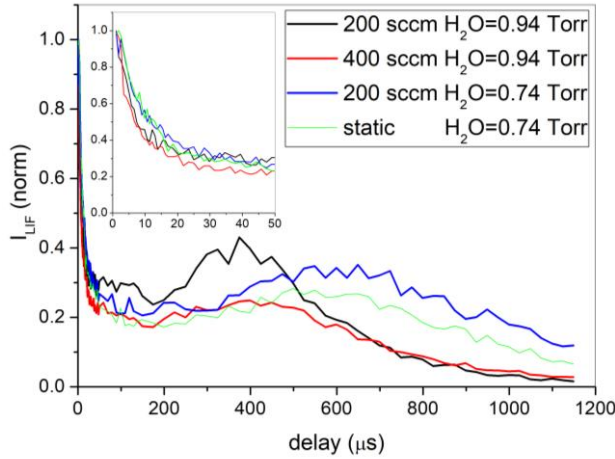


Fig. 6 [OH] decay at different flow conditions. The LIF signal is normalized to the value at the post-discharge time $t_{pd} = 2\mu s$.

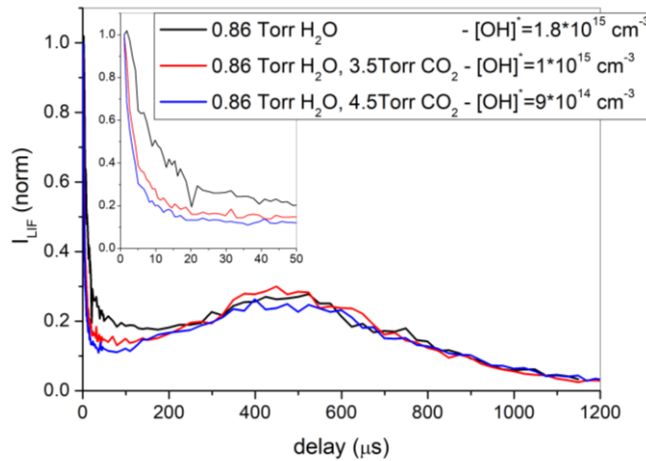


Fig. 7 [[OH] decay after the first pulse of the burst ($N_b=1$) with addition of CO_2 . The total pressure is 760 Torr. The LIF signal is normalized to the value at the post-discharge time $t_{pd} = 2\mu s$. $[OH]^*$ is the [OH] absolute value at $t_{pd} = 2\mu s$.

A similar decay behaviour in the post-discharge was observed in [1]. In that paper, the current pulse was about 200 ns long, while no info was given on the discharge pulse energy. Similar to our findings, an [OH] maximum in the post-discharge around 200 μs was found, but only on addition of a small O_2 quantity to the He- H_2O mixture. Based on the results of a 0-D kinetic model, without a discharge kinetic model, the authors in ref. [1] concluded that the reaction $O + OH \rightarrow O_2 + H$ causes quenching of OH and production of increased densities of H, HO_2 and

H_2O_2 , with subsequent additional production of OH in the late afterglow. Our results indicate that the production of the precursors of OH reforming depends on water content, it undergoes a built-up with successive pulses, although at present limited to the second pulse only, and it is not affected by the presence of moderate CO_2 amounts. It is clear that a complete kinetic model is needed to interpret these findings. Conversely, it is also clear that a variety of conditions can be achieved that will be very useful for the validation of kinetic models. In particular, we underline that the number of pulses in the burst is an additional parameter that can influence the discharge and post-discharge kinetics. Here we have explored only one inter-pulse delay, 350 μs , that is the minimum period allowed by the actual HV pulse generator. It will be highly interesting to change this value, in particular decreasing it down to few microseconds, in order to observe more marked build-up phenomena. Work is in progress in this direction.

5. References

- [1] Verreycken T and Bruggeman P J 2014 Plasma Chem. Plasma Process. **34** 605 - 619