

# Simulation Chamber Study of Night-time Chemistry of Aldehydes and PANs

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## Introduction

Aldehydes are major secondary products of the atmospheric oxidation of most of the volatile organic compounds (*Carlier et al, 1986*). Their night-time reactivity with  $\text{NO}_3$  could lead to the production of related peroxyacylnitrate (*Cantrell et al, 1986*). However, the kinetic database for the reactions  $\text{NO}_3 + \text{RCHO}$  is still inconsistent and the need of absolute measurement has been pointed out (*Wayne et al, 1991*). On the other hand, the night-time chemistry of the peroxyacyl radicals could be of importance in the night-time production of OH radicals (*Canosa-Mas et al, 1996*). Simulation chamber experiments were conducted together with numerical simulation to investigate the full mechanism of the degradation of formaldehyde, acetaldehyde and propionaldehyde.

## Experimental

All the experiments were performed in a  $0.977 \text{ m}^3$  pyrex simulation chamber of 6 metres length which has been described elsewhere (*Doussin et al, 1997*). The reactor is equipped with IR and UV long path mirror system of 108 and 72 m optical path lengths, respectively. Both long path in-situ FTIR and UV-visible DOAS measurements were used in order to perform absolute studies by measuring the concentrations of both VOCs and  $\text{NO}_3$ . The concentrations were monitored by UV spectrometry at 662 nm for the nitrate radical and by FT-IR spectrometry for others  $\text{NO}_y$  and organic compounds.

$\text{NO}_3$  was produced by mixing NO and  $\text{O}_3$  in a small flow reactor connected to the chamber.

## Methods

Model calculations that include 63 reactions in the case of acetaldehyde and 93 in the case of propionaldehyde were performed for each experiment and the unknown rate coefficients were determined by fitting the model results to the experimental data (*Doussin, 1998*). The comparison between model results and experimental data is shown in Figs 1-2.

## Results and discussion

The results are relevant of three main scientific fields : reactivity of NO<sub>3</sub> with aldehyde, reactivity of NO<sub>3</sub> with peroxyacyl radicals and heterogeneous chemistry of peroxyacyl radicals.

a) The mechanistic studies of the reaction of aldehyde with NO<sub>3</sub> have confirmed that these processes proceed exclusively via overall H-atom abstraction on the aldehyde group. Under our experimental conditions (low NO level due to ozone concentration - see Figs 1-2) the PANs yield reach rapidly 25-35%.

The kinetic results of the first step of these processes are reported in Table 1-3.

Table 1. : Rate constant of the reaction NO<sub>3</sub> + HCHO - Comparison with previous works.

T° (K)	k(NO <sub>3</sub> + HCHO) molec <sup>-1</sup> cm <sup>3</sup> s <sup>-1</sup>	k(NO <sub>3</sub> + HCHO) updated * molec <sup>-1</sup> cm <sup>3</sup> s <sup>-1</sup>	Source NO <sub>3</sub>	References
298±1	(3.2±0.2)x10 <sup>-16</sup>	(5.0±0.4)x10 <sup>-16</sup>	N <sub>2</sub> O <sub>5</sub>	Atkinson et al, 1984
298	(6.3±1.1)x10 <sup>-16</sup>	-	O <sub>3</sub> +NO <sub>2</sub>	Cantrell et al, 1985
298	(5.4±1.1)x10 <sup>-16</sup>	-		Hjorth et al, 1988
298	(8.0±1.5)x10 <sup>-16</sup>	(5.4±1.0)x10 <sup>-16</sup>	O <sub>3</sub> +NO <sub>2</sub>	Hannachi, 1986
296	(5.2±0.9)x10 <sup>-16</sup>	-	O <sub>3</sub> +NO <sub>x</sub>	This work

\* Data updated from new reference values in case of relative rate study.

Table 2. : Rate constant of the reaction NO<sub>3</sub> + CH<sub>3</sub>CHO - Comparison with previous works.

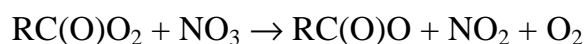
T° (K)	k(NO <sub>3</sub> + CH <sub>3</sub> CHO) molec <sup>-1</sup> cm <sup>3</sup> s <sup>-1</sup>	k(NO <sub>3</sub> + CH <sub>3</sub> CHO) updated * molec <sup>-1</sup> cm <sup>3</sup> s <sup>-1</sup>	Source NO <sub>3</sub>	References
300	(1.2±0.3)x10 <sup>-15</sup>	(2.8±0.7)x10 <sup>-15</sup> *	NO <sub>2</sub> + O <sub>3</sub>	Morris et al, 1974
298±1	(1.3±0.3)x10 <sup>-15</sup>	(2.1±0.4)x10 <sup>-15</sup> *	N <sub>2</sub> O <sub>5</sub>	Atkinson et al, 1984
299±1	(2.1±0.4)x10 <sup>-15</sup>	-	N <sub>2</sub> O <sub>5</sub>	Cantrell et al, 1986
298	(2.74±0.07)x10 <sup>-15</sup>	-	N <sub>2</sub> O <sub>5</sub>	Dlugokenski et al, 1989
298	(2.1±0.7)x10 <sup>-15</sup>	-	O <sub>3</sub> +NO <sub>x</sub>	This work

\* Data updated from new reference values in case of relative rate study.

Table 3. : Rate constant of the reaction NO<sub>3</sub> + C<sub>2</sub>H<sub>5</sub>CHO - Comparison with previous works.

T° (K)	k(NO <sub>3</sub> + C <sub>2</sub> H <sub>5</sub> CHO) molec <sup>-1</sup> cm <sup>3</sup> s <sup>-1</sup>	Source NO <sub>3</sub>	References
298	(5.7±0.4)x10 <sup>-15</sup>	N <sub>2</sub> O <sub>5</sub>	D'Anna et al, 1997
298	(4.5±0.9)x10 <sup>-15</sup>	O <sub>3</sub> +NO <sub>x</sub>	This work

b) The reactions between NO<sub>3</sub> and peroxyacyl radicals have been added to the mechanism.



A third in-situ generation of nitrate radical was performed when the PANs concentrations were high and aldehydes concentrations were low. As can be seen from Fig. 2, when the NO<sub>3</sub> concentration increases, PAN decomposition rate increase. It is well known that the reaction

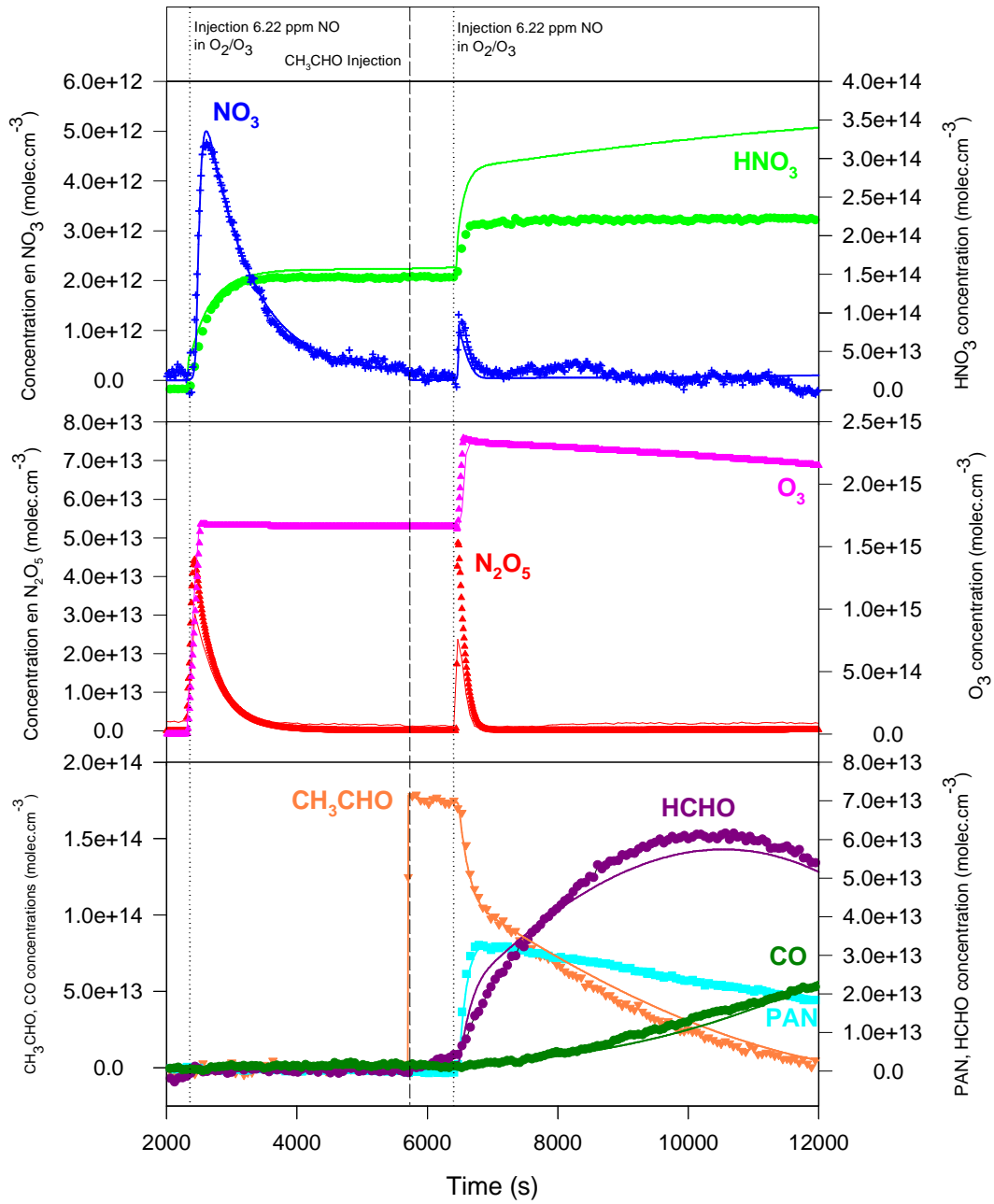


Fig1 : Experimental (thin line) and model (bold line) results. Concentration time behaviour without and with acetaldehyde (2 stages experiments)

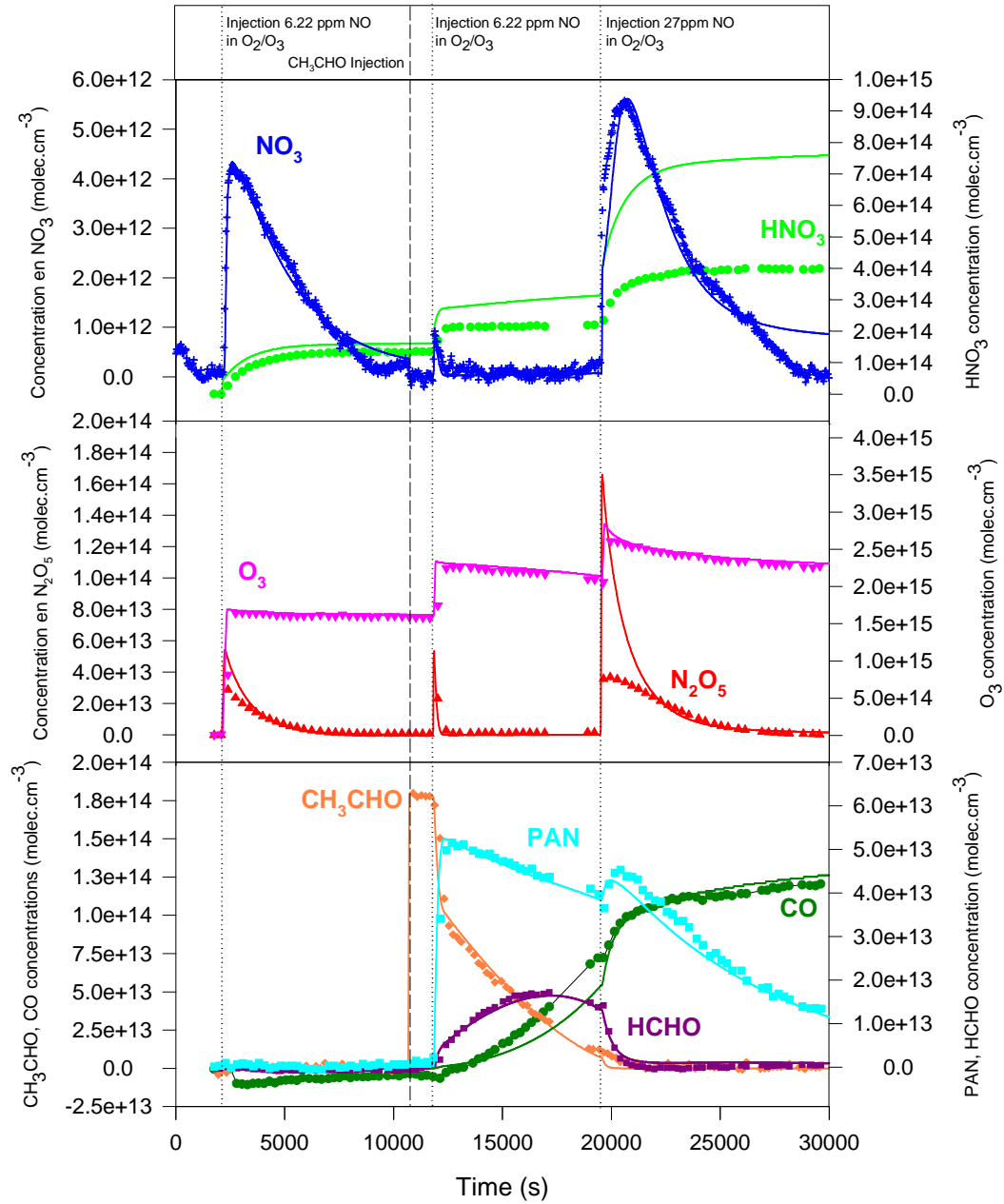


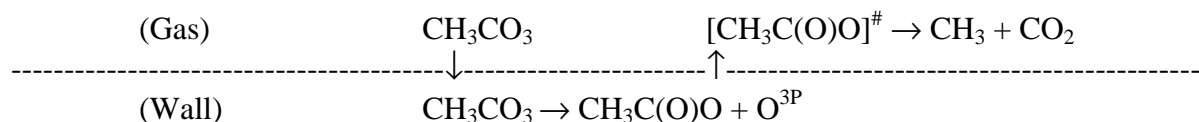
Fig. 2 : Experimental (thin line) and model (bold line) results. Concentration time behaviour without and with acetaldehyde (2 stages experiments) followed by a third generation of NO<sub>3</sub>.

of PANs with NO<sub>3</sub> is very slow so this result is the first evidence of a reaction between peroxyacyl radicals and nitrate radicals under simulated tropospheric conditions. This procedure allowed us to study for the first time under atmospheric conditions these important reactions and to determine the associated rate constants with a good sensitivity of the fit.

Table 4. : Rate constant of the reaction NO<sub>3</sub> + peroxyacyl - Comparison with previous works.

T° (K)	k(NO <sub>3</sub> + CH <sub>3</sub> CO <sub>3</sub> ) molec <sup>-1</sup> cm <sup>3</sup> s <sup>-1</sup>	Method	References
300-403	20x10 <sup>-12</sup>	Slow flow reactor - preliminary study	Biggs et al, 1994
403-443	(4±1)x10 <sup>-12</sup>	Flow reactor	Canosa-Mas et al, 1996
295±2	(3.2±1.4)x10 <sup>-12</sup>	see text	This work
T° (K)	k(NO <sub>3</sub> + C <sub>2</sub> H <sub>5</sub> CO <sub>3</sub> ) molec <sup>-1</sup> cm <sup>3</sup> s <sup>-1</sup>	Method	References
298±2	(2.5±1.2)x10 <sup>-12</sup>	see text	This work

c) We took into account the wall reactions of peroxyacyl radicals (Schurath et al, 1979) in order to simulate our experimental data. In accordance with Langer et al (Langer et al, 1992) the following process was considered.



The adsorbed oxygen atom could then react with the adsorbed nitric acid to give OH and NO<sub>3</sub>. The pseudo first order rate parameter of this process was found to be highly variable with the wall conditioning. Considering a S/V ratio of 9 m<sup>-1</sup> for our reactor, the value 0.1.s<sup>-1</sup> < k<sub>1st</sub> < 7.s<sup>-1</sup>. are in good agreement with the previous results of Langer et al (Langer et al, 1992).

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