

## ***Interactive comment on “Implementation of an IBBCEAS technique in an atmospheric simulation chamber for *in situ* NO<sub>3</sub> monitoring: characterization and validation for kinetic studies”***

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First of all, the authors would like to thank the anonymous referee for this discussion and its constructive comments, corrections and suggestions that ensued. We have carefully replied to all its comments and the paper has been improved following its recommendations. All technical corrections suggested by the referee have been carefully performed. Answers have also been provided for all comments and changes have been performed accordingly. Please find below the answers to the comments:

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1. The kinetics analysis ignores any loss of NO<sub>3</sub> other than bimolecular reaction of NO<sub>3</sub> with Alkene. This is most probably an over simplification. For example, what about wall loss, there could also be diffusion outside of the analysis region. Using a simple model, the addition of a first order loss of NO<sub>3</sub>, still results in a straight line from a plot of the change in alkene vs the product of [alkene].[NO<sub>3</sub>] delta t (as in figure 8), however the retrieved rate coefficient is lowered and this impact gets worse as the wall loss increases. So if there is wall loss the retrieved rate coefficient does not equate to the bimolecular rate coefficient. How have the authors taken into account wall loss or any other first order loss process? Have they modeled their system? Can they show what the quantitative impact on the retrieved rate coefficient will be? Have they made any attempt to evaluate first order losses of NO<sub>3</sub>?

We may have not explained clearly enough the kinetic method, because it appears that the referee did not understand it. NO<sub>3</sub> is indeed subject to losses other than the reaction with the VOC, for example wall losses in the chamber, reaction with NO<sub>2</sub>, with peroxy radicals... Nevertheless, this method consists of monitoring the decay of the trans-2-butene and not the one of NO<sub>3</sub>, and this decay is plotted as a function of [VOC]x[NO<sub>3</sub>]xdt. Here, [NO<sub>3</sub>] is measured with the IBBCEAS technique as a function of the time (and not modelled), so we don't care about additional loss processes. What is important here is the measured concentration of NO<sub>3</sub> radicals by the time the consumption of the VOC is measured. So, NO<sub>3</sub> can be consumed by other processes without affecting the result. But if the VOC is consumed by other loss processes (e.g. wall losses), this could affect the results. For this reason, trans-2-butene stability has been checked before every oxidation, and no significant loss beside dilution was observed. It allowed the authors making the hypothesis that trans-2-butene was only consumed by reaction with NO<sub>3</sub>.

2. The authors claim that there is good agreement with literature, however, their rate coefficient is the fastest that has been reported in the literature. Also, given that this rate coefficient is probably not simply the rate coefficient for the bimolecular process, most

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probably a lower limit as result of other first order loss proves, the true bimolecular rate coefficient in their system is likely to be even faster. Faster rate coefficients normally worry kineticists, if one looks at the absolute rates reported in table 3 the unweighted average is  $3.87 \times 10^{-11}$  with a standard deviation of  $0.12 \times 10^{-11}$  i.e. statistically the reported rate coefficient is higher than the current experimental database. Can the authors explain why this is the case?

We are a bit surprised by this comment. Isn't  $(3.87 \pm 0.12)$  in agreement with  $(4.13 \pm 0.78)$ ? Agreement between values has to be considered by taking into account the uncertainties, otherwise it has no sense. And by taking them into account, our determination is in agreement with the unweighted average of absolute determinations and with the IUPAC recommended value. But it is also in agreement with all individual absolute determinations. The only disagreement which has been noticed is with relative determinations which are significantly lower than other determinations and where not taken into account for the IUPAC recommended value. In conclusion the authors affirm that our determination is in good agreement with literature.

3. In Table 1, Deff is given as 82 which is simple the geometric distance, if I am not mistaken. Will that be the case? A purge flow is used to protect the mirrors and this will impact the effective path length, this is also likely to be a function of pressure and flow of purge gas. Have experiments been performed to quantify the Deff as a function of purge gas flow rate and pressure?

All experiments presented here were performed without a purge flow so the effective distance was considered to be the geometric distance (82 cm). A sentence clarifying this statement has been added in the manuscript (P.2.2 L.111): "Nitrogen flush was not used in this study, but is available for further type of experiments. " Nevertheless, experiments have been conducted to quantify the impact of purge gas flow and pressure:

- Due to nitrogen purge, pressure is only slightly rising: the purge flow is 300 mL min<sup>-1</sup>, and 300 mL represents a variation of 0.03 % of the total volume of the chamber.

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This flow is compensated by the sampling of measurement instruments. No pressure variation was ever measured due to the purge gas flow. Nevertheless, characterization experiments using a known NO<sub>2</sub> concentration were conducted, in order to quantify the impact of major pressure variation on the pathlength. They showed no significant impacts of pressure on the pathlength. Pressure variations of 10 mbar in the chamber lead indeed to decrease of the path length of less than 1 %.

- Using also a known concentration of NO<sub>2</sub>, experiments have been performed by adding different flows of purge, in order to determine an efficient flow, i.e. which does not induces a major decrease of the pathlength and a progressive dilution in the measurement area. They showed that the optimal flow is 300 mL min<sup>-1</sup>, because it efficiently protects the mirrors and induce no long term dilution. With this flow, Deff is decreasing to 62 cm (as it is written in the manuscript L.110), adding an uncertainty of 5 % to the nitrate radical concentration. A sentence to explain these experiments has been added in the manuscript P.2.2 L.108: "This flow rate has been optimized in order to efficiently protect the mirrors while limiting the dilution of the mixture in the measurement area."

4. On line 290 the authors state "these parameters were therefore precisely monitored during the experiment leading to the value of  $2.17 \times 10^{-11}$  cm<sup>3</sup>.molecule<sup>-1</sup> at 298K and at 1030 mbar." Is that the value of the equilibrium constant? If so, what are the errors? They need to be stated. Can the authors show that within experimental error that agrees with those reported in Atkinson et al., 2004, indeed how does it compare to the recommended IUPAC /JPL recommended values?

The value of  $2.17 \times 10^{-11}$  cm<sup>3</sup>.molecule<sup>-1</sup> is indeed the equilibrium constant. This value was not measured in our study, but calculated using the parametrization recommended by the IUPAC (Atkinson et al., 2004) at a pressure and temperature which were measured during the experiments. So, here, it appears that there is a misunderstanding. By "parameters", we mean temperature and pressure and not the rate constant. In order to make it clearer, the sentence has been modified P.4 L. 305 in the

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manuscript: "These two parameters were therefore precisely monitored during the experiment allowing calculating an equilibrium constant of  $2.17 \times 10^{-11} \text{ cm}^3 \cdot \text{molecule}^{-1}$  at 298K and at 1030 mbar, using IUPAC database parameters (Atkinson et al., 2004)."

5. In Figure 6, the authors report linear regression between the FTIR and the BBCEAS. Can they provide errors on the slopes? Also include a description of those errors, e.g. are they 1 sigma just from the linear fit, or do they take into other experimental errors?

Errors on the slopes are now provided. The values were calculated to be  $1.0 \pm 0.2$  for NO<sub>2</sub> and  $1.1 \pm 0.3$  for NO<sub>3</sub> by considering the statistical error on the slope, which is twice the standard deviation, and the sum of the systematic relative errors on FTIR and IBBCEAS measurements. To explain it, sentences have been written in P.4 L.313: "Here, the overall uncertainty was calculated as the sum of the statistical error on the slope (twice the standard deviation, 4 %) and systematic errors on FTIR (i.e. on I<sub>B</sub>-NO<sub>2</sub>, 4 %) and IBBCEAS measurements (which includes uncertainties on NO<sub>2</sub> cross sections and on the mirrors reflectivity, 9%)." and in P.4 L.320 "The error is calculated with the same method as for NO<sub>2</sub>".

6. Finally what are the absolute errors on the rate coefficient? The authors report a simple error analysis based on the line of best fit, i.e. what is the total error? The authors need to take into account errors in flows, absorption cross section etc etc

The authors have considered that the statistical error, calculated as twice the standard deviation on the linear regression and which takes into account the dispersion of the experimental points, is mainly due to spectra treatment uncertainties. However, we agree that this statistical error does not include systematic ones, such as errors on cross sections. So we have added the uncertainty on NO<sub>3</sub> concentration. As described in the manuscript, this uncertainty was estimated to be 9% and corresponds to the sum of NO<sub>2</sub> and NO<sub>3</sub> cross sections errors and the uncertainty of NO<sub>2</sub> concentration for reflectivity measurement. By summing the statistical error (10%) and the uncertainty on NO<sub>3</sub> concentration (9%), we obtain an overall uncertainty of  $0.78 \times 10^{-13} \text{ cm}^3$

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molecule-1 s-1. This has been corrected in the manuscript L.391 and in Table 3. It must be noticed that because trans-2-butene concentration is both on x and y axes, the error on I<sub>B</sub>I is not considered here. An explanation has been added P.5 L.392: "The uncertainty on the rate constant was estimated as the sum of the relative uncertainties on NO<sub>3</sub> concentrations and twice the standard deviation on the linear regression."

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