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Discussions

Interactive comment on "Implementation of an IBBCEAS technique in an atmospheric simulation chamber for *in situ* NO$_3$ monitoring: characterization and validation for kinetic studies" by Axel Fouqueau et al.

Anonymous Referee #2

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The paper reports on the implementation of an IBBCEAS technique for the detection of NO3. A few questions arise

1. The kinetics analysis ignores any loss of NO3 other than bimolecular reaction of NO3 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 NO3, still results in a straight line from a plot of the change in alkene vs the product of [alkene].[NO3] 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 NO3?

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 coefficent is probably not simply the rate coefficient for the bimolecular process, most 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 3.87×10^{-11} with a standard deviation of 0.12×10^{-11} i.e. statistically the reported rate coefficient is higher than the current experimental database. Can the authors explain why this is the case?

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?

4. On line 290 the authors state "these parameters were therefore precisely monitored during the experiment leading to the value of 2.17×10^{-11} cm3.molecule-1 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?

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?

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

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