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Comment on acp-2021-1021

Christa Fittschen

Community comment on "OH and HO₂ radical chemistry at a suburban site during the EXPLORE-YRD campaign in 2018" by Xuefei Ma et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-1021-CC1>, 2022

Comment of Christa Fittschen to

"OH and HO₂ radicals chemistry at a suburban site during the EXPLORE-YRD campaign in 2018"

It is interesting to notice that you observe the same increasing disagreement between modeled and measured OH concentration with decreasing NO concentrations. You say that the disagreement is probably not due to interference in the FAGE system, because using the chemical modulation system did not show any significant interference. Unfortunately, these experiments were carried out on June 7, which, looking at Figure 3, was a day where measurements and model were in very good agreement. So, it seems that no strong conclusion on absence of interferences in your FAGE system can be drawn from these observations.

It might have escaped from your attention that our group has identified a new OH interference in our FAGE system which would be able to explain such increasing disagreements between measured and modeled OH concentrations with decreasing NO: the product of the reaction between RO₂ and OH radicals, trioxides ROOOH, leads in our FAGE system unequivocally to an OH signal¹. Even though the lifetime of such trioxides and with this their absolute concentration is not known, this interference has the characteristics needed to explain your observation: the turnover of the reaction of RO₂ + OH (and thus the ROOOH concentration) increases with decreasing NO concentration.

Even though not clearly stated, but I guess the reactions of RO₂ + OH are not included in your reaction mechanism. This class of reaction has now been studied several times^{f.e.2-3} and it is admitted that the rate constants are fast. Your Figure 8 allows to make a rough estimation on the importance of this class of reactions under your conditions: in the afternoon, the RO₂ loss is dominated (>50 %) by their reaction with HO₂. Taking the rate constant of RO₂ + HO₂ as >10⁻¹¹ cm³s⁻¹ and the rate constant of RO₂ + OH as 10 times faster (>10⁻¹⁰ cm³s⁻¹), one can estimate that with 100 times less OH compared to HO₂ (Figure 4), around 5% of the RO₂ radicals will be lost through reaction with OH. It is admitted that the reaction of large peroxy radicals with OH leads nearly exclusively to the formation of ROOOH⁴, it can therefore be supposed that a non-negligible steady-state trioxide concentration can build up.

From these rough estimations it seems interesting to update your model by integration of $\text{RO}_2 + \text{OH}$, add a reasonable loss process for the trioxides and check for correlation of trioxide concentration and degree of disagreement between measurement and model.

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