Atmospheric Chemistry and Physics Discussions

Atmos. Chem. Phys. Discuss., referee comment RC2
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Comment on acp-2021-449

Anonymous Referee #2

Referee comment on "Atmospheric oxidation of *α*,*β*-unsaturated ketones: kinetics and mechanism of the OH radical reaction " by Niklas Illmann et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-449-RC2, 2021

This is a very nice laboratory experimental study of the kinetics and mechanism of the reactions of OH with 3-methyl-3-penten-2-one and 4-methyl-3-penten-2-one. Kinetic data on Cl + the same two unsaturated ketones is also presented. The experiments and analysis are of high-quality (though the non-use of standard numerical integration tools is surprising) and clearly presented. I have only minor comments, which are listed below.

L21 RONO2 is one type of organic nitrate but so is PAN. Perhaps simply write "Based on the calculated product yields an upper limit of 0.15 was determined for the yield of RONO2....."

L37 isoprene is not the most abundant NMHC (as it is very reactive) but has the highest emission strength

L45 can you provide an estimate of the impact of the loss of α,β-unsaturated ketones on ozone and SOA formation ?? my guess is that it is not significant.

L47 replace “proving” with “identifying” ?

L48 under which (NOx) conditions are formaldehyde and methyl glyoxal the main oxidation products ?

L56-61 This text, describing a method that is not used, should be removed.

L67 PAN levels depend on the temperature and levels of e.g. NO, but not PAN formation

L74 In the Table, the reference column needs to be altered so that it is clear what the “this work” references actually refer to

L90 “Cleanliness is proved by FTIR” ? Perhaps “purity was confirmed by FTIR” is better.

L112 “Reactants and products are basically monitored using in-situ FTIR spectroscopy”. Delete “basically”.

L148 suppress

L151 replace "infolds" with "contains"

L173 The assumption that the wall loss rate is the same when the lights are on and when the lights are off should be mentioned. With fluorescent lamps (which get warm when on) this is often not the case as the glass walls are heated during operation which leads to convection and thus more rapid transport of gases to the walls.

L179 "An average value of the cross sections given by Profeta et al. (2011) and Talukdar et al. (2011) has been used for methyl glyoxal". Please justify this. How different are the results of the two studies cited ?

L191 2.7 Modelling. This is a peculiar (outdated) approach to the problem. It would be interesting to know why none of the commonly used numerical integration programs were used such as KINTECUS (freeware for academia). I encourage the authors to recheck their results using such a program.

L207 "loss" = loss rate ?

L222 "If pseudo-first order conditions are proven by the experimental data...." Please indicate how this is evaluated (exponential decay ??)

L317 3.2 Infra-Red cross sections

L354 "more" = "moreover"

L373 3.3.1 3-Methyl-3-penten-2-one + OH

L374 "Figure 2 shows evaluation details of IR spectra...." Delete "evaluation details"

L374 replace "product study experiment of 3M3P2" with "during an experiment to examine product formation in the OH-initiated oxidation of 3M3P2"

L392 replace "no remaining absorptions" with "no remaining IR absorption features"

L425 replace "3.3.2 4-Methyl-3-penten-2-one" with "3.3.2 4-Methyl-3-penten-2-one + OH"

L496 replace "under both experimental and atmospheric conditions" with "in the present experiments and in the atmosphere"

L516 "While photolysis of methyl glyoxal is the main loss process under most atmospheric daytime conditions the OH reaction dominates in the present experimental system.". Please do the calculation and compare J-$CH_3C(O)CHO$ with k(MGLY)*[OH] for the present experiments.

L612 "become only relevant at" . What does this mean ? At what temperature would a non-negligible fraction of ROONO2 be present ?

L638 "the potentially formed RONO2 species could also be subject of significant photolysis". Please assess this properly. What are the cross-sections of RONO2 at the photolysis wavelengths likely to be. As CH_3ONO is used as OH source, there is presumably good overlap with the lamp-spectra. The same applies to the loss via OH. What do you expect the loss rate to be for the available OH concentration ?

L653 "would suffer from a dense chemical environment around Cα". I've no idea what this statement means. Please re-phrase.