Atmospheric Measurement Techniques Discussions

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Reply on RC3

Magdalena Vallon et al.

Author comment on "LED-based solar simulator to study photochemistry over a wide temperature range in the large simulation chamber AIDA" by Magdalena Vallon et al., Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2021-362-AC3, 2022

First of all we thank the reviewers for their constructive comments. Our answers are given in the following always directly after the individual comments in bold letters. Furthermore, corresponding modifications in the manuscript are given in parentheses.

Line 35-36: Odd way of saying that light enables photochemical pathways that are not available by merely increasing the temperature. Rephrase.

Answer: We agree and modified the sentence as follows:

"From a chemical viewpoint, light enables, besides the thermodynamic, photochemical pathways by specific electronic excitation of the molecules."

Line 39-40: This sentence is vague in the way it is written. The authors provide examples in the next paragraph but I would rephrase this sentence to be more specific.

Answer: We agree and modified the sentence as follows:

"Various photochemical reactions like the formation of ozone and OH-radicals or the fragmentation of halocarbon compounds have been studied widely in the last few decades, now offering a good understanding for many photochemical reactions of atmospheric relevance. However, for many of the multiple organic compounds in the atmosphere additional research is still needed (Goldstein, 2007)."

Line 43: Should read "In principle"

Answer: We changed this accordingly.

Line 125: Did the experiments after using NO2 differ in any way?

Answer: The photolysis of 2,3-pentanedione in the presence of NO_2 did not show a significant difference compared to those without. We could not identify any interaction of NO, NO_2, or O_3 with 2,3-pentanedione or its photolysis products.

Figure 4: j(NO_2) seems fairly constant even though the emissions profiles are quite

different in Figure 3. For figure 3 electrical settings were adjusted, is that the same case for Figure 4? If so it should be stated.

Answer: Although the UV light intensities increased for lower temperatures as indicated in figure 3a, the measured j(NO_2) did not increase significantly, at least not for the lowermost temperature of 213 K. This is somewhat surprising and may partially be due to a not completely representative intensity measurement at low temperatures. These measurements were done through a window at the bottom of the chamber and may have a small bias due to temperature dependent reorientations. Furthermore, the NO_2 photolysis is dominated by the higher photon fluxes and absorption in the visible spectral range.

Line 305 and Figure 5: How consistent are kW values? Did they change with temperature? Also, did the authors perform exclusively wall loss experiments?

Answer: No exclusive wall loss experiments were done for 2,3-pentanedione. We used the time periods before and after the photolysis experiments to determine the wall losses. The differences between the wall losses observed before and after the photolysis were used to estimate their uncertainties. These differences decreased with decreasing temperatures and so the uncertainties we estimate.

Figure 6: Formaldehyde and acetaldehyde yields increase with temperature, is this the result of faster wall losses artificially reducing the yields? Or increased adsorption leading to different product distributions? The suggested changes to alkoxy radical chemistry are a plausible reason but there could be other reasons.

Answer: Indeed, there could also be other reasons. However, the uncertainties resulting from the wall losses are included in the uncertainties of the yields.

Figure 9: Figure S7 and lines 435-440: The authors mention that product formation for the DTDP photolysis experiments is slower at lower temperatures but the photolysis rate is the same. Any explanation for this? Figure S7 only shows one temperature.

Answer: We don't find a significant change of the DTDP photolysis rate with temperature but a weaker formation of the two products potentially due to changing branching ratios for reactions following the photolysis.

Line 460: Should read pinene

Answer: corrected.

Line 463: Numbers should be subscript

Answer: corrected to NH_4NO_3.