Atmospheric Chemistry and Physics Discussions

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Comment on acp-2021-424

Anonymous Referee #1

Referee comment on "An assessment of the tropospherically accessible photo-initiated ground state chemistry of organic carbonyls" by Keiran N. Rowell et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-424-RC1, 2021

Rowell and co-authors present a theoretical assessment of photo-initiated ground-state chemistry in carbonyls, and discuss the potential importance of various reaction pathways for tropospheric chemistry. Some of these pathways are not generally considered in current models and could be of chemical relevance. The topic is certainly suitable for ACP. Since I am not a theoretical chemist I can offer no perspective on the reliability of their approach or the level of theory employed -- I leave that to other reviewers to assess. With that caveat, I found the paper of high quality, thorough, and a pleasure to read. I expect the results to be a useful step towards improved resolution of this class of reactions in atmospheric models. I recommend publication and have only a few minor suggestions for the authors' consideration.

Numbering below refers to the line numbers in the manuscript.

Title, since the entire paper focuses on carbonyls I recommend including that term in the title.

Table 1, why are a few values given uncertainties but others are not? Do I understand from the footnotes that some reported values in this table are from previous work while the remainder are from the current study? If so I recommend making that distinction more clearly in the table.

16, "For example, small carbonyls, which rank at the top of anthropogenic emissions". Please be more precise. Do you mean these are the top anthropogenic VOC emissions? The top anthropogenic carbonyl emissions? The top anthropogenic emission of any species?

18, “emitted as biological volatile organic compounds (BVOCs) that oxidise to carbonyls”. Note that carbonyls can also be emitted directly by plants.

22, “As there are…” this sentence is somewhat awkward and difficult to parse, consider rephrasing

44, I believe the citation here should refer to the GEOS-Chem model, not to the Harvard atmospheric chemistry group.

Section 1.1. This is a great description and explanation of the processes following UV absorption, well done.

162, Figure referenced here should be S3

180, reactant here should include R (or R’) to match the product

383, “Photo-initiated keto–enol tautomerisation has only been observed in acetaldehyde (Clubb et al., 2012; Shaw et al., 2018)”. While this section of the paper is specific to saturated aldehydes, I think this statement could create confusion and should be clarified – i.e., acetaldehyde is the only saturated aldehyde in which this has been observed. As pointed out later it has also been observed in acetone and MVK.

464, “This suggests…” I find the wording in this sentence unclear, consider clarifying

522, “Molecular hydrogen is an important atmospheric reducing agent”, please specify what you mean here