

Atmos. Chem. Phys. Discuss., referee comment RC2  
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## Comment on acp-2021-424

Anonymous Referee #2

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Referee comment on "An assessment of the troposphericly 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-RC2>, 2021

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This manuscript discusses a wide range of high-energy isomerisation and fragmentation reactions of carbonyl compounds, based on the data from quantum chemical calculations. The authors conclude that many product channels are energetically accessible for photochemically excited intermediates, and propose that such pathways may be of importance in the atmosphere.

This work is of very high quality, with an extensive set of reliable quantum chemical calculations discussed in a clear and accessible manner, and with well laid-out argumentation how these results support the authors' premise of possible contribution of chemistry on the ground state potential energy surface after excitation by absorption. The results are thought-provoking, and if shown to be important in the real atmosphere the proposed pathways represent a departure from our current mechanistic understanding of photochemistry, and could be an important addition to atmospheric kinetic models.

The only significant comment I have on this paper is that, while the authors show that ground state chemistry can occur and may be important, they can not show how important it is. With only energetic data available, it can only be determined that a reaction is accessible, but without an assessment of the reaction entropy the rate of the chemical reaction can not be determined and hence no estimate of the yields can be made. Reactions of highly excited intermediates in the ground state through high-energy exit channels has been proposed several times already, but most of the time appears to be of very minor importance as the energy-specific rate coefficients are typically very low. Specifically, the highly excited intermediate has a high state density at those internal

energies, while the transition state has a high barrier and hence a low amount of excess energy, leading to a low state density and thus low reaction rates. The threshold argumentation of the authors is therefore only qualitative (a nuanced version of pass/fail), but does not provide any evidence that these reaction can be sufficiently fast to have a non-negligible impact.

I suggest that the authors more explicitly state that their data does not allow for an assessment of the reaction kinetics and yields, and that their conclusions are thus rather tentative. Alternatively, the authors could use simple RRKM theory with the already available quantum chemical data to calculate approximate energy-specific rates for one or more of the most promising channels and compare those to the collision rate to support their premise. Quantitatively correct master equation studies are not necessary for this paper.

Overall, I find this paper to be highly interesting, highly relevant, very well written, and an excellent basis for further research on this intriguing topic. I support publication after minor changes.

Specific comments:

The title overstates the scope of the paper somewhat, as it is not shown how important the reactions are, merely that they are accessible.

The authors use the word "threshold" throughout, but this is ambiguous and it is not clearly defined what is meant. For an endothermic reaction, the threshold energy is the product energy, as tunneling can allow reaction below the TS barrier. The authors seem to

refer mostly (but not always?) to the barrier height as the threshold.

p. 2, line 25 "...carbonyls... are one of the few classes of VOC that can absorb solar radiation in the troposphere". Many VOC can, but they are very poor at it (and/or have no reaction pathways in that energy range). I propose adding "efficiently".

figure 3: "carbohydrate" is perhaps not the best descriptor of this class. "Hydroxy-aldehyde", supplementing the "linear aldehyde" and "branched aldehyde" classes might be more descriptive.

p. 5, line 106: "Although these isomers are theoretically accessible at actinic energies, their formation barriers are very high with low barriers for the reverse isomerisation."

This needs one or more references.

p. 6, line 113: "The calculated S0 thresholds are used to determine general trends..."

Threshold energies (here apparently used as product energies) are only one aspect in the contribution of a channel. I suggest the authors also discuss entropy (or TS rigidity), and TS barrier height.

p. 11, line 230: "All but the smallest decrease in threshold are outside the likely accuracy

of the B2GP-PLYP-D3 calculations." This may be interpreted to say the opposite of what is meant? Rephrase to say that the energy differences exceed the expected uncertainty on the calculations, except for the smallest 2 kJ/mol value.

p. 16, line 295: It may be worthwhile to mention that the keto-enol tautomerization is greatly enhanced by catalysis by acids and other mobile-H compounds.

p. 18, line 334: "... the threshold... is ~13 kJ/mol lower...". After rounding that should be 14 kJ/mol. Also, the So et al. value of 298.7 kJ/mol is not significant to 4 digits, and representing that value as "299 kJ/mol" here could make sense.

p. 19, line 352: "Triple fragmentation has been observed as a primary photolysis mechanism in propanal and 2-methylpropanal, with QYs of 4% and 9%, respectively, at 1 atm pressure of N<sub>2</sub>" (and similar statements elsewhere).

The observation of low yields of the products does not imply that these products are formed from S<sub>0</sub> chemistry, and the authors do not state that the literature has unequivocally documented that these products are not formed from the S<sub>1</sub>/T<sub>1</sub>/... excited states. This section needs to state explicitly for each observation cited that it is known/shown that the products are from S<sub>0</sub>, or that it is not (yet) clear that S<sub>0</sub> has a significant contribution in these observations.

p. 20, line 283: "Dissociation of the aldehyde reduces its concentration and hence reduces the rate of enol formation."

It reduces the yield of enols, but the rate (rate coefficients) remains the same.

p. 22, line 467-471

Fast reversible keto-enol isomerisation increases the accessible state density at the higher energies, and hence lowers the effective rate of the other (higher-energy) channels by decreasing the effective concentration of the carbonyl in favor of a reservoir as enol. It is thus not a given that these channels have no influence on the importance of the other channels.

p. 23, line 505: "In both polluted and pristine regions there are discrepancies between the predictions of atmospheric models and field measurements of the concentrations of organic acids"

For your information: a recent paper by Franco et al. (DOI: 10.1038/s41586-021-03462-x) proposes a pathway that may close the gap.

Supporting information: use the more exact terms "product energy" or "reaction barrier" rather than "threshold". If both TS and product energies are available, it could be worthwhile to show both.

Typos:

Several instances of "formaldehydye", "glycolaldehydye", "crotonaldhyde"

p. 21, line 433: space between "2CO"