Atmospheric Chemistry and Physics Discussions

Atmos. Chem. Phys. Discuss., referee comment RC2
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Comment on acp-2021-553

Anonymous Referee #2

Referee comment on "Investigations into the gas-phase photolysis and OH radical kinetics of nitrocatechols: implications of intramolecular interactions on their atmospheric behaviour" by Claudiu Roman et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-553-RC2, 2021

The study presented here, analyses the photolysis and OH reaction of four different nitrocatechol compounds. Kinetic data have been obtained at atmospheric temperature and pressure conditions by a relative rate technique using dimethyl ether, cyclohexane, and methanol as reference compounds. The reaction rate constants of the nitrocatechols with OH have been reported here for the first time. In addition, the photolysis frequencies of 3-nitrocatechol and 5-methyl-3-nitrocatechol were determined. The values indicate that photolysis is the dominant loss process for these two compounds under atmospheric conditions.

The structural properties of the four nitrocatechol compounds are discussed and the influence of the substituent position on the OH reactivity is analysed. In general, the abundance of a nitro group deactivates the aromatic ring. The observed nitrocatechols show reaction rate constants with OH that are up to two orders of magnitude smaller than reaction rate constants of catechols without an attached NO_2 group. The nitro group withdraws electrons from its -ortho and -para positions thus deactivating these positions and weakening the O-H bond. In 3-nitrocatechol compounds, an intramolecular H-bond between -OH and nitro group can be observed in the IR spectra. In general, reaction rate constants for the reaction of nitrocatechols with OH predicted by SAR seem to overestimate measured data. The manuscript provides substantial information for further SAR improvements.

I recommend the manuscript for publication after the minor comments have been addressed.

General questions:

Which OH concentrations are typically reached in the chamber?

L122: How large are wall losses compared to photolysis?

L143: Can you be more specific? How large is the fraction which reacts with OH and how large are the contributions of dilution and wall loss compared to that?

Could you add figures for the photolysis experiments?

Did you perform any additional product measurements?

Minor and technical comments:

Sometimes you write HO instead of OH (e.g., L.46., L100). Please check throughout the manuscript for consistency.

L53: Nitroaromatic compounds (NAHs) -> I would call it ''Nitroaromatic hydrocarbon (NAH) compounds''

L71: is of great concern of interest -> is of great interest

L116: Please give a reference for the k2 values that you used for the three reference compounds.

L126, L182, L254, L263: Why is the division sign used here? It is not common everywhere to use it to give a range of value. Maybe you can use an alternative.

L184: coefficient

Fig. 7, panel A: please specify in the description, why you use the two different symbols for the OH attack sites

Fig. 7, panel B is not referenced in the text. Where exactly do you want to use it?

Check references for the use of subscript (e.g., NO_2, NO_3)