

We would like to thank the Editor and the anonymous referee for considering our manuscript as suitable for publication in ACP after minor revisions.

Editor's comments:

“The important question raised by referee 2 regarding the use of a linear fit to describe data that is clearly not following a linear trend in Fig. 2B has not been satisfactorily addressed. I see no discussion of the non-linear nature of the data in the manuscript, or why a linear fit was used for a portion of the data. This needs to be discussed in the main text as well as mentioned in the figure caption. There should also be a discussion as to possible causes for the clear non-linear trend of observed nitrophenolate production. If you were to exclude the first data point for zero reaction you would get a different linear fit that would better describe that portion of the data. It may be reasonable to use a simple linear fit as an /approximation/ for some portion of the data but this needs to be clearly stated and discussed. You should also explain why you do not use a non-linear function that could likely well describe all of the data obtained. There is likely some interesting chemistry occurring that explains the non-linear nature of the data in Fig. 2B and a discussion of this would strengthen the manuscript. Please be sure to properly discuss this through further revisions to your manuscript.”

Our responses to the comments provided together with the changes made in the revised manuscript are provided below.

***Referee 2 comment:***

Figure 2B is using a linear fit to calculate the yield and a statistical analysis was carried out to show that this analysis was valid. However, by eye this is not a linear trend as there is clear curvature. Why were the points that are used selected to represent the linear portion? Please expand the analysis to show the variation found when a different range of initial points are used to provide uncertainty values for the assumptions that are made here

**Author's response:** To gain more insights into the underlying mechanisms of the 4NP+OH reaction a kinetic box-model was constructed.

The modeling results revealed that the non-linear trend observed in Fig. 2A was due to secondary reactions of the products formed (primarily 4NC) with the OH. This is an expected behavior of the plots derived via eq. 1 (Gierczak et al., 2021). For this reason, the yields (slopes) are derived from the initial portion of such plots via linear regression model; such a procedure is generally accepted for deriving realistic formation yields of a given product(s). Applying a different regression model and excluding the point of origin (0,0) from the regression analysis would certainly yield a better fit to the experimental data but results of such non-linear fitting cannot be connected with the mechanism of the reaction under investigation.

However, to reproduce the experimental data presented in Fig. 2B, the kinetic model had to be modified to include regeneration of 4NC from 4NC + OH with the yield of 0.5. The mechanistic implications of these findings are now discussed in section 3.1. A new, important conclusion obtained from the kinetic modeling is that the deprotonation of the precursor may enhance the disproportionation reaction of the nitrocyclohexadienyl-type radicals.

We agree that the behavior of the plots derived via eq. (1) was not sufficiently discussed in the manuscript.

**Changes in the revised manuscript:** Fig. 2 was revised, results of the linear fitting were removed. Instead, the modeled yields of 4NC generated by the kinetic box model are now included in Fig. 2A and Fig. 2B.

**Caption of Fig. 2** was revised as "The formation of phenolic products from the 4-nitrophenol (A, pH=2) and 4-nitrophenolate (B, pH=9) + OH reaction. The molar yields for 4NC were estimated from the initial sections of the plots via linear regression analysis (Fig. S4 and Table S3). Plots derived with eq. (I) for the products quantified are expected to curve during the course of the reaction because these molecules are also reactive towards OH. The lines for 4NC are results of kinetic modeling (Table S3 and Fig. S5)."

**Section S5** was added in the SI, containing results of the linear regression analysis, and the description and the results obtained from the kinetic box model. Modeling results are now referenced in the main text. The curving of the plots obtained via eq. (I) is reproduced by the box model developed, thereby confirming that their behavior is due to the secondary reactions of 4NC with the OH.

Results of the kinetic modeling was incorporated in the discussion connected with **Figs. 2 and 3** in the main text.

**Fig. 3** in the main text was revised due to minor formatting and editorial mistakes.

## Literature

Gierczak, T., Bernard, F., Papanastasiou, D. K., and Burkholder, J. B.: Atmospheric Chemistry of *c*-C<sub>5</sub>H<sub>7</sub>F and *c*-C<sub>5</sub>F<sub>8</sub>: Temperature-Dependent OH Reaction Rate Coefficients, Degradation Products, Infrared Spectra, and Global Warming Potentials, 125, 1050-1061, 10.1021/acs.jpca.0c10561, 2021.

Gierczak, T., Bernard, F., Papanastasiou, D. K., and Burkholder, J. B.: Atmospheric Chemistry of *c*-C<sub>5</sub>H<sub>7</sub>F and *c*-C<sub>5</sub>F<sub>8</sub>: Temperature-Dependent OH Reaction Rate Coefficients, Degradation Products, Infrared Spectra, and Global Warming Potentials, 125, 1050-1061, 10.1021/acs.jpca.0c10561, 2021.

Herrmann, H., Schaefer, T., Tilgner, A., Styler, S. A., Weller, C., Teich, M., and Otto, T.: Tropospheric Aqueous-Phase Chemistry: Kinetics, Mechanisms, and Its Coupling to a Changing Gas Phase, *Chem. Rev.*, 115, 4259-4334, 10.1021/cr500447k, 2015.

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