Response to the Reviewer's Comments

October 15, 2025

1 REFEREE REPORT

Comment: Although it is not clearly stated in the manuscript, it seems that the authors don't seem to see any stabilization of the RCs or the PCs. In that case, the values used for the LJ parameters are not particularly relevant to the conclusions of this paper. Nevertheless, to avoid future confusion for other authors, I note that the LJ parameters reported here are strange, and the description of how they are calculated seems incomplete. The words suggest that they directly calculate the LJ parameters for the RC...N_2 interaction. But then, how can the size, sigma (which presumably represents the distance between the center-of-mass of the RC and N_2 at the minimum of the complex) be only 2.6 Å, when the separation between the CI and the HONO in the RC itself is on the order of 3 Å? This makes no sense. Also, if they are directly calculating the LJ parameters for the RC...N_2 interaction then why do they report values for the bath gas alone. Those values shouldn't even enter into the kinetic analysis.

Reply: The reviewer is correct that we did not find any stabilization of the RCs or the PCs. We thank the reviewer for pointing out the discrepancy in the LJ parameters, which were due to a high error in the fitting parameters. In the revised manuscript, we have refined the fitting to reduce the error. We now obtain reasonable LJ parameters within an acceptable level of MUD. The newly fitted ϵ and σ values are 895.5 K and 3.1 Å, respectively. The reviewer is also correct that there is no need to report the LJ parameters of the bath gas; therefore, in the revised manuscript, we have removed that sentence from the methodology section.

Comment: The authors should report what value they presumed or calculated (I still can't tell if it was calculated or presumed-it seems like it must be the latter since no data is provided for its MEP) for the capture rate for the process from products to the

PC complexes. Or do they not include this process in their master equation and simply presume the PC complexes dissociate?

   Reply: We would like to clarify that the capture rate for the process from the products to the PC complexes was obtained using the ILT method. We have now provided the corresponding rate in Table S10 of the ESI. The fitted Arrhenius parameters derived from these rate values were used in the master equation calculations.

Comment: At line 269 the authors state that "keff increases only slightly". I think this should say "keff decreases only slightly" since the context of the sentence is for increasing temperature.

   Reply: We have now rectified that sentence in the revised manuscript.

Comment: The left-hand y-axes in Figure 5 need some improvement.

   Reply: As per refere's advice, we have refined the left-hand y-axes of Figure 5.