

Interactive comment on “Does acetone react with HO₂ in the upper-troposphere?” by T. J. Dillon et al.

Anonymous Referee #3

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The paper describes a laboratory study of the reaction between acetone and HO₂ and a modeling study assessing the contribution of this reaction to acetone degradation in the upper troposphere. The experimental studies monitor HO₂ indirectly detecting the OH product of the HO₂+NO reaction. Given the large discrepancy between two recent theoretical studies of this reaction this study represents a reasonable attempt to resolve the discrepancies between the prior work. These experiments are not easy to perform at the lowest temperatures that are reported here. The difficulty here is that, in the absence of the ability to directly monitor HO₂, the authors are attempting to model a poorly constrained system and they acknowledge this. They have chosen to fix the rate of the adduct + NO reaction by analogy with another peroxy reaction and use the forward addition rate from Hermans et al. to model the data. The results clearly seem to show evidence for reaction between HO₂ and acetone at the lowest temperature of the C6965

experiments but the attempts to quantify the results are, in my view, rather more problematic. I don't think it is reasonable to arbitrarily fix two out of three rate coefficients and then report “measured” equilibrium constants. Having spent a limited time running simulations of the chemistry, I find that these simulations are very sensitive to the value of the adduct+NO reaction and yet the authors assign an uncertainty of $\pm 50\%$ to this reaction although it has never been measured. It also appears that a little more could have been done to constrain some of these rate coefficients. The authors state that in all experiments, a large excess of $[\text{NO}] > 1 \times 10^{14}$ molecule cm^{-3} was available to irreversibly trap (R2) the product peroxy radical, and prevent re-dissociation (R-1) to products. However if their estimate of R2 is correct the trapping rate coefficient at 207K would be $\sim (1.5 \times 10^{-11} \times 1.5 \times 10^{14}) \sim 2250 \text{ s}^{-1}$. This is the same as their estimated dissociation rate so all the adduct molecules would not have been scavenged. It would have been informative to examine the pressure dependence of the OH temporal profiles at higher NO concentrations. If in fact the adduct was being completely scavenged then a pressure dependence in the adduct formation rate might be discernable. Overall I think this work merits publication. It certainly resolves the very large discrepancies in the calculated rate coefficients reported in the recent theoretical studies and suggests that the actual rate coefficient is much closer to the value calculated by Hermans et al. It also appears to show that the equilibrium constant calculated by Hermans et al. is not consistent with the experimental data. I think the authors underestimate the uncertainty in their equilibrium constants but it is difficult to see how this uncertainty could be large enough to encompass this difference. This is critical in assessing the atmospheric implications since it changes the reaction from an important acetone sink to one that is of no significance. I think that inclusion of the temporal profiles in the supplementary material would be extremely useful. It is very difficult to assess a paper like this without repeating the numerical simulations and access to the all the temporal profiles would be a great help.