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Title: Temperature dependent rate coefficients for the reactions of the hydroxyl radical with the atmospheric biogenics isoprene, α -pinene and D-3-carene

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Reviewer: A. J. Hynes, University of Miami

I am submitting this review without reading other reviews/comments and I apologize for any duplication. This is a high quality determination of the rate coefficients for the reactions of OH with isoprene, α -pinene and δ -3-carene. Temperature, pressure and bath gas dependencies are measured. The work certainly merits publication but I have a couple of comments that relate to the isoprene study. The difference between the value reported here and two prior "low values" reported by my research group are small with current measurement of 9.3 ± 0.4 overlapping our 2004 value of 8.5 ± 0.6 within the stated uncertainties. I absolutely concur (perhaps self-servingly) with the conclusion that the current IUPAC recommendation is too high. Because of the importance of this reaction in the atmosphere the accuracy and precision of determinations is very important and in the case the difference between the Mainz and Miami work is clearly associated with the value of the absorption coefficient used for in-situ monitoring of reactant concentration. I believe than in-situ monitoring improves the precision of rate coefficient determinations and, as noted in the paper, a subsequent resolution of the discrepancies in the absorption coefficients allows the rate coefficient to be updated. The abstract contains the statement:

"These results indicate that significant discrepancies between previous absolute and relative rate determinations of k_1 result in part from σ values used to derive the isoprene concentration."

However it seems to me that the difference in σ values only explains the difference between the direct studies from Miami and Mainz, I don't see it having any bearing on the other direct and relative rate studies.

It should be noted that in our work we measured cross sections and rate coefficients for both normal and deuterated isoprene and the spectra were almost identical but with a slight blue shift in the deuterated spectrum. This, however, produced significantly different cross sections at the 228.8 nm Cd atomic line that was used to monitor concentrations in our work. The cross section we measured at 215.5 was within 4% on an old study by Jones and Taylor. I suspect than in this case it may be easier to measure the rate coefficient than the absorption cross-section. We obtained the same rate coefficient (within experimental error) for both compounds and felt this was consistent with an addition to a double bond i.e. there should not be a kinetic isotope effect.

I should also note that both of the papers:

Campuzano-Jost, P., Williams, M. B., D'Ottone, L. and Hynes, A. J.: Geophys. Res. Lett., 27, 693, 2000.

Campuzano-Jost, P., Williams, M. B., D'Ottone, L. and Hynes, A. J.: J. Phys. Chem. A, 108, 1537, 2004.

contain several confusing errors about the actual wavelength that was used to monitor concentration. As the corresponding author this was my responsibility and I apologize to others, including the current authors, who had to decipher this. It was, as noted above, the 228.8 nm Cd atomic line.

For reactions (2) and (3) that reported values confirm and extend the current literature database.

Again, this is a high quality study that merits publication.