

## ***Interactive comment on “Daytime tropospheric loss of hexanal and *trans*-2-hexenal: OH kinetics and UV photolysis” by E. Jiménez et al.***

**Anonymous Referee #1**

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General comments: This paper presents measurements of the UV absorption cross sections from 250–370 nm and OH radical rate constants as a function of temperature for hexanal and *trans*-2-hexenal. This is an important area of research in atmospheric chemistry, as the fate of oxygenated VOCs in the atmosphere and their contribution to the free radical budget in the troposphere are not well characterized. There have been relatively few measurements of the UV absorption cross section for these compounds, and although there have been previous measurements of the OH radical rate constants at 298 K, there have not been any previously reported measurements of the temperature dependence for these reactions.

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1) The OH radical rate constants were made using pulsed laser photolysis of  $\text{H}_2\text{O}_2$  as the OH radical source, resulting in estimated maximum OH radical concentrations on the order of  $10^{12}\text{cm}^{-3}$  with  $\text{H}_2\text{O}_2$  and aldehyde concentrations on the order of  $10^{14}\text{cm}^{-3}$ . Under these conditions, reactions of OH radicals with  $\text{H}_2\text{O}_2$  are a significant loss of OH, and the authors correct for this in their analysis by subtracting the first-order loss rate of OH due to reaction of  $\text{H}_2\text{O}_2$ , measured in the absence of aldehyde, from measurements of the overall first-order loss rate. However, there is no discussion of potential interferences from secondary reactions of OH with reaction products given these radical concentrations. I am assuming that the authors obtained the pseudo-first-order rate constant from an exponential fit of their observed decays to equation 4, but there are no examples of the measured first-order decays to give the reader confidence in this approach. The authors should include example pseudo-first-order decays and fits in their discussion of the OH kinetics measurements, as well as a discussion of potential interferences from secondary OH radical chemistry.

2) The authors really only measure the UV absorption cross section for these compounds, and assume that the overall quantum yield is 1 for their estimation of the photolysis rates (the reference to the previous measurement of the absorption cross section of trans-2-hexenal of O'Connor et al. is not included in the reference list). Did the authors observe any degradation of the aldehydes during their photolysis experiments? The authors measured a small difference in the concentration of each aldehyde after leaving the reaction cell. Was this difference independent of laser power in their experiment? Based on their measured absorption cross sections and photolysis, would they expect a significant loss of aldehyde in their experiment?

3) The authors briefly discuss the mechanism for the OH radical reactions of these compounds, suggesting that the higher rate constant for the OH + trans-2-hexenal reaction was due to the contribution of OH addition to the double bond. However, the observed negative temperature for this reaction is similar to that observed for the OH + hexenal reaction, where the dominant mechanism is likely to involve hydrogen

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abstraction from the aldehyde group through the formation of an OH addition complex. Would one expect a similar temperature dependence if the OH addition channel was occurring to a significant effect? Is the different reactivity between hexanal and trans-2-hexenal consistent with structure-activity relationships? The manuscript would benefit from an expanded discussion of the mechanisms and the potential products of the OH-initiated oxidation of these compounds.

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Interactive comment on Atmos. Chem. Phys. Discuss., 6, 13225, 2006.

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