

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

Anonymous Referee #3

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This paper adds to our knowledge of rate constants for OH + unsaturated aldehydes, specifically *trans*-2-hexenal. The work on hexanal is somewhat less novel as previous studies of the room temperature OH reaction rate constant are in agreement and the absorption cross-sections have been published previously. The kinetic study is carefully done and points out the need for care in kinetic studies of unsaturated carbonyl compounds, more generally. Unfortunately, the calculated photolysis rates for *trans*-2-hexenal are misleading because the quantum yield for photolysis (as opposed to photoisomerization) is known to be nearly zero.

The kinetics study is the strength of this paper. I suggest the authors highlight the need to measure the concentrations of flowing *trans*-2-hexenal rather than using concentrations determined from the flow rate of a mixture of vapor in inert gas. This may

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be necessary, generally, for kinetic studies of many of the unsaturated carbonyls and alcohols that have recently drawn the interest of atmospheric chemists. Presumably, trans-2-hexenal polymerizes on the walls of the sample bulb. In addition, at the end of section 2.2.1, rather than saying optical measurements "were preferred," it would be clearer to say that they "were used."

In comparing their rate constants to those previously measured, the authors might want to emphasize the apparent absence of pressure effects on the rate constant. The might also emphasize the fact that this is the first temperature dependent study of the OH + hexenal rate constant. Both these aspects are relevant for understanding the mechanism of OH + aldehyde reactions and building structure-activity relationships.

One aspect of the method for the kinetic study appears less than ideal: the filter for detection of OH emission has a band pass of 150 nm FWHM, and so is not terribly specific to OH. Could there be fluorescence from the aldehydes?

The low quantum yield for photolysis of trans-2-hexenal appears to be known to the authors. They cite the work of Plagens for the "photoisomerization" of trans-2-hexenal to cis-2-hexenal. Although I do not have the conference paper cited, Plagens dissertation is available (<http://elpub.bib.uni-wuppertal.de/edocs/dokumente/fb09/diss2001/plagens;internal&action=buildframes.action>). It is clear that cis-trans isomerization is the dominant photoreaction path for both isomers. Therefore, photoabsorption results in little or no net loss of 2-hexenal. The work of O'Connor, et al., on trans-2-hexenal cited in footnote 1 was published in Physical Chemistry Chemical Physics (2006, 8, 5236-5246) just days before submission of the manuscript under discussion. O'Connor, et al., confirm the dominance of photoisomerization with a quantum yield of 0.36 for the trans isomer. Photodissociation appears not to be needed in their mechanism. Unless the atmospheric fate of the cis isomer is (or is thought to be) very different from that of the trans isomer, it seems misleading to treat photoisomerization as a loss process.

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O'Connor, et al., obtain absorption cross-sections for trans-2-hexenal that are slightly higher than those reported here. It may be important to note that O'Connor found it necessary to continuously flow their sample of trans-2-hexenal to avoid losses in the optical cell. Unfortunately, in the present manuscript the absorption cross-sections were measured using static rather than flowing samples. In all other respects these measurements appear to have been carefully done.

The use of a unity quantum yield to determine the lifetime of hexenal is also questionable, as values much less than unity are known. Moortgat (Pure Appl. Chem., Vol. 73, pp. 487-490, 2001) reports a value of 0.28 for hexenal.

The quantum yield reported by O'Connor, et al., would suggest that the value of J_2 measured by Plagens, et al., should be much lower than that calculated in the manuscript using an assumed quantum yield of unity, yet the values are in good agreement. Do the authors have any thoughts on this apparent discrepancy?

As a result of the work of Plagens and of O'Connor, the Abstract needs editing to remove (or heavily edit) discussion of the importance of photolysis for trans-2-hexenal and the claim of having the "first-reported" absorption cross-sections. Similar editing is necessary in the Conclusions. J -values in Table 3 should be recalculated and the upper part of Figure 5 re-drawn. The lower part of Figure 5 can be deleted.

Some small issues: 1) Finlayson-Pitts and Pitts (2000) is cited in the text but does not appear in the Reference section. 2) The description of the apparatus for measuring cross sections is somewhat awkward. The manuscript refers to an "irradiation source" or "photochemical source" when "light source" would be less misleading (since there is no intention of doing photochemistry). 3) It would be appropriate to report the repetition rate used for the lasers. 4) It seems unnecessary to discuss the potential photodissociation paths of hexenal (R1a - R1c), since the manuscript does not address photolysis products or quantum yields. 5) The English could use polishing, but is sufficiently clear. 6) Absorption cross sections were said to be determined from "weighted

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averages." The weighting factors are not described.

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