

Interactive comment on “Rate coefficients for the gas-phase reaction of OH with (\vec{Z})-3-hexen-1-ol, 1-penten-3-ol, (\vec{E})-2-penten-1-ol, and (\vec{E})-2-hexen-1-ol between 243 and 404 K” by M. E. Davis and J. B. Burkholder

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Response to the comments by anonymous referee #2 on ACPD-2011-11

We thank the anonymous referee for taking their valuable time to review our manuscript and making constructive comments. We have addressed the comments in our revised manuscript as specifically outlined below.

Referee Comment: For (E)-2-penten-1-ol and (E)-2-hexen-1-ol, it doesn't appear that any tests for OH regeneration were conducted at high temperature? Can this process

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be entirely ruled out in these cases? (Regeneration might be most favorable at elevated temperature?)

Response: It is correct that OH regeneration tests were only performed at room temperature and below for these two compounds as outlined in the data summary tables. On the basis of our experimental measurements alone the possibility of some OH regeneration at high temperature can't be ruled out completely. However, the rate coefficient data for these reactions followed Arrhenius behavior very well over the range of temperatures included in our study. This would argue, although indirectly, that OH regeneration was not occurring at the elevated temperatures included in our study. More extensive tests were performed for the other two compounds included in this study in which Arrhenius behavior was also observed and no measurable OH regeneration was found.

Referee Comment: The observation of different reactivity for the E- and Z- isomers is an interesting and valuable one, and I have just a few suggestions to help clarify the discussion. First, the 2001 Papagni et al. paper presents evidence that the enhancement factor for –OH substituents is closer to a factor of two, rather than the value of 1.6 given by Kwok and Atkinson, and I would suggest using this updated value in the calculations performed and discussed. Further, I don't think the SAR calculation for (Z)-3-hexen-1-ol currently includes an effect for the presence of the OH functionality. Given the discussion in Papagni et al. (and confirmed here), that the position of the OH group relative to the double bond is not critical, would it not make sense to include the enhancement for the (Z)-3-hexen-1-ol SAR calculation as well?

Response: The work of Papagni et al. found that the OH group enhancement factor in unsaturated alcohols is 20% greater than previously thought (Kwok and Atkinson estimated an enhancement factor of ~1.6 for the –CH₂OH group) and that the enhancement is not critically dependent on the relative position of the OH group. The present work is in agreement with that conclusion. The SAR calculated rate constants given in our paper used the Kwok and Atkinson estimated value for the enhancement factor. We

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have revised the text to acknowledge and to use the updated Papagni et al. enhancement factor. We also now include the OH enhancement in the SAR calculation for (Z)-3-hexen-1-ol. The revisions provide a more updated discussion, but do not change the conclusions from this work. The text in the discussion section was revised as follows (revisions underlined): “The room temperature rate coefficients for the reaction of OH with (E)-2-penten-1-ol and (E)-2-hexen-1-ol can be compared with the values predicted using the structure activity relationships (SAR) of Kwok and Atkinson (1995) combined with updated enhancement factors for the –CH₂OH and –CH₂CH₂OH groups from the work of Papagni et al. (2001). The SAR estimated rate coefficients for reactions 3 and 4 are identical since the reactivity factors for C₂H₅ and C₃H₇ are the same. The SAR estimated rate coefficient is 1.33×10^{-10} cm³ molecule⁻¹ s⁻¹, which is approximately twice the experimentally measured values of $(6.76 \pm 0.70) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ and $(6.15 \pm 0.75) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. Note that the rate coefficient measured in our work for the shorter chain length molecule is actually greater. The level of agreement between the SAR estimate and the experimental values is probably within the acceptable range for the SAR estimation method. The SAR rate coefficient for the OH + (Z)-3-hexen-1-ol reaction is in good agreement with the experimental value, to better than 10%, while the SAR rate coefficient for the 1-penten-3-ol reaction is only ~15% less than the experimental value.”

Minor editorial comments: pg. 2378, line 2 – there is a period after the structure of 3-hexen-1-ol that should be deleted.

Fixed

Pg. 2379, line 18 – please insert a comma after ‘onion’.

Done

Pg. 2383 – ‘determined’ would be better than ‘performed’.

Agree. Changed

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Pg. 2387, line 1 – should be ‘obey’ rather than ‘obeys’, I think.

Changed

Pg. 2387, line 22 – should be “(E)-2-hexen-1-ol” (also line 4 on following page).

Corrected

Pg. 2392, line 11 – Lifetimes between about 2.5 to 5 hrs. might be more accurate, for the OH concentration given?

Agree. The text has been revised to include a range of lifetimes.

Table 6 – last compound listed in the table title should be (E)-2-hexen-1-ol.

Corrected

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 2377, 2011.

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