

General comments:

The paper reports the results of a carefully conducted study of three OH reactions important for atmospheric/environmental science along with the analysis of the available data. The subject is relevant to *ACP*. The quality of the obtained data are excellent and the adequate discussion of the experimental procedure, data treatment and results obtained is provided. A manuscript can be accepted for publication in *Atmospheric Chemistry and Physics* after minor revision. Below are comments authors may consider and address in preparation the final version of the manuscript.

Specific comments:

Page 4, line 12: Using the “head-space above a liquid sample”, i.e. the vapor/gas phase of the sample is potentially a source of an error, especially when impurities in the sample are not identified. The vapor phase can be substantially enriched with more volatile impurities thus affecting results of both spectral and kinetic measurements. The stated purity of reactants (Aldrich) characterizes a bulk liquid sample whereas the amount of impurities in the vapor phase can be substantially different. So, it is always a good idea to use liquid sampling to prepare reactants.

Page 4, lines 13-16: This is confusing a bit. Condensation onto optical windows as well as other surfaces may occur in both cases of using pure compound and diluted mixture. However, when working with pure compound we are aware of the concentration in the gas phase (pressure control), at least. Using absorption cells of different optical path length allows to check for such condensation. When working with diluted mixtures, we do not minimize the potential condensation problem. Moreover, we have no idea on the compound concentration in the gas phase if such condensation occurs. Of course, similar results obtained with two approaches would prove the absence of the problem.

Page 6, line 26: Once small “error” is mentioned, it would be useful to clarify if this is about one st. err., two st. err., 95% confidence interval or anything else.

Page 6 (Eq. 2), page 8 (Eq. 4), Figures 5, 8 and through the text: This is entirely up to authors’ discretion because it is simply supporting mathematics. However, why not to use different symbols for different parameters in Eq. 2, Eq. 4, and through the text? At least, “ E/R ” is widely used in the Arrhenius equation (Eq. 4) by both kinetic data makers and users.

Page 7, line 1: Why “scatter” is here? This is probably “change” or “variation” due to variation of laser energy.

Page 7, line 18 and later through the text: Using “non-Arrhenius temperature dependence” to name the temperature dependence, which follows an Arrhenius expression, Eq. 4, with the positive B seems very confusing for a gas kinetic paper. The “non-Arrhenius temperature dependence” or non-Arrhenius behavior is rather associated with deviations of the observed data from the Arrhenius dependence given by Eq. 4 in the manuscript. Actually, this “inconsistency” appears in the authors’ text. Authors present Eq. 4 as “Arrhenius expression” (page 8, line 26) and use it in deriving the result. In page 11 lines 21-22 authors declare “non-Arrhenius dependence” derived... from the fit of the Arrhenius

expression (Eq. 4) to their data. I would rather suggest using the commonly accepted “negative E/R ” or authors’ “negative B ”.

Page 7, line 30: How those “two studies of $k_1(298\text{ K})$ conducted at lower pressures indicated that the high pressure limit was close to 3 Torr and 1 Torr”?

Page 8, line 5: This is not exactly correct statement. The value (8.47 ± 0.59) overlaps with the range of IUPAC recommendation of $8.7 < k_1(298\text{ K}) < 1.15$. It actually barely overlaps even with the value reported in the present work, (9.3 ± 0.4).

Saying this, it would be beneficial for the discussion of IUPAC recommendation if the IUPAC recommended uncertainty interval is also shown in Figure 5.

Page 8, line 18: It would be useful to clarify why results of these particular studies are shown in Figure 6. One could guess that only data obtained over the temperature range are shown, but the single room temperature data point reported by Spangenberg et al., 2004 is also shown here.

On the other hand, data from Park et al. are not shown in Figure 6 although they are discussed below (lines 22, 25) and in the figure caption (page 22, lines 6-7).

Page 8, line 25: IUPAC indicates 249-348 K as the temperature range of Siese et al., not 249-438 K. Which one is correct? Also, this paper (from Eurotrac Symposium) is not listed here. Does it make a sense either to list it in the references or not to mention in the discussion?

Page 8, lines 15-17 and 31-33: Authors suggest re-evaluation of k_1 and its uncertainty based on their new data and corrected data from Campuzano-Jost et al., 2004. However, the current IUPAC recommendation is based on results of numerous studies, which yield both the recommended k_1 and the uncertainty to overlap the published data chosen for evaluation. I am not going to say that the authors’ recommendation makes no sense, but it definitely needs more discussion of the available data, which is probably beyond the scope of this work. So, I would rather suggest a softer statement “probably can be reduced”.

Page 10, line 29 and page 11, line 12: The “black dot-dash line” represents two different data sets – page 25, line 28 and page 11, lines 12-13. Is there any mistake here? In any case, the description of this line (or two lines) is missing in both Figure 9 and the figure caption.

Page 11, line 28: The statement “... $k(T)$ approaching the collision limit” does not seem very accurate. Authors found that both rate constants increase exponentially with $1/T$; however, there is nothing indicative of approaching to any limiting value yet.

Page 31, Figure 9: The pink dotted line is described as Gill & Hites in the legend but not shown in Figure 9. Comments on “black dot-dash line” are above (page 10 line 29...)

Page 11, lines 25-34: Finally, the following is rather discussion/speculations than a comment... Whereas one can expect both reactions to be similarly fast to a zero approximation, their rate constants are not supposed to be equal. To a first approximation, one can consider both compounds, α -pinene and Δ -3-carene, as derivatives from 1-methylcyclohexene with some possible “steric restrictions” shading π -electrons of the reactive C=C site. (See their molecular structures, for example, in webbook.nist.com). Moreover, the C=C site is “hidden” a bit better in case of alpha-pinene with the $(\text{CH}_3)_2\text{C}\langle\text{CH}_2$ cluster located out of plane and closer to the reactive C=C.

Based on these speculations, one could expect the rate constant decreasing from 1-methylcyclohexene to Δ -3-carene (k_3) and to α -pinene (k_2). This is consistent with now available data: 9.8×10^{-11} from Aschmann et al., 2012 and $k_3 = 8.1 \times 10^{-11}$, $k_2 = 5.4 \times 10^{-11}$ from the present study. Thus, the values of k_2 and k_3 determined in the present study seem very reasonable or, better to say, they support the above speculations.

Technical corrections:

Title: It seems like semi-column is missing after “biogenics” – it should be either “...the reactions of the hydroxyl radical with the atmospheric biogenics: isoprene, alpha-pinene...” or “...the reactions of the hydroxyl radical with isoprene, alpha-pinene ...”.

Page 2, line 14: It seems like something is missing here. I can guess that it was supposed to be as “... Stone et al., 2011) **with** the greatest discrepancies...”

Page 7, line 18: Figure **6**, not Figure 5.

Page 8, line 26: Figure **6**, not Figure 8.

Page 9, line 28: Table **3**, not Table 2.

Page 9, line 31: “using an absorption cell with the path length of 43.8 cm” would be more appropriate.

Page 10, line 3: Table **2**, not Table 1.

Page 10, line 7: Table **3**, not Table 2.