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Ms. Title: Rate coefficients for the reactions of OH radicals with C3-C11 alkanes determined by the relative rate technique.

General Comments:

The authors report room temperature and temperature-dependent rate coefficients for OH radicals with a series of C3 – C11 alkanes (straight-, branch-chain, and cycloalkanes), using a relative rate technique. They have also looked into the bath gas effect on the measured rate coefficients and they have compared their results with literature data, where available, and structure reactivity relationships (SAR) estimates. Although the results from this work are worth to be published there are some major and some minor issues that need to be addressed before acceptance. One of the major concerns of the present reviewer is related to the lack of physical interpretation of the observed differences in k values in some reactions when N_2 was used as bath gas. Further, for the majority of the studied reactions, there are available data in the literature. It is not a problem to provide additional kinetic data, but this makes sense when there is a thorough study that provides more accurate data or addresses problems of previous studies. In this work, the reason for doing that is not justified, and studying so many compounds at once does not improve data quality. **Suggestion:** Maybe publishable after major revisions.

General Comments:

1. *Abstract*, ln. 15. Please correct “reported were determined” with “reported was determined”
2. It is highly recommended the authors to correct the rate coefficient capital K throughout the manuscript to avoid confusion with the reaction equilibrium constant. Please use k to refer to the reaction rate coefficient.
3. Please avoid using rate constant since k is not a constant, particularly since the authors have also measured the rate coefficient temperature dependence ($k(T)$). Although rate constant is commonly used it would be better to be more accurate.
4. Please replace ‘ $\text{cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ ’ with ‘ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ’ throughout the text.
5. Please replace $\text{OH}\cdot$ and $\text{NO}_3\cdot$ with OH and NO_3 radical throughout the text.
6. Pg. 2, ln. 47–50. The reason that OH abstraction reactions dominate atmospheric degradation is related to both the faster reactions OH radical initiate along with the relative abundance of the oxidants. So, the at least 5 orders of magnitude slower reactions that NO_3 radical initiate

need to be combined with the relative abundance of OH and NO₃ radical during daytime. Please include a sentence to address that or, even better, remove the whole discussion with NO₃ chemistry, since it is out of the scope of this study.

7. Pg 3. Ln. 63–67. The statement in which relative rate and absolute methods are compared (stated twice in the document) is misleading. First, absolute rate measurements are not that rare, and time-resolved measurements have been extensively and very efficiently used in the past by some of the leading groups on kinetics studies. The recommendation of the present reviewer is to either rephrase or delete this argument (in both places), particularly since the two different techniques have advantages and disadvantages that are not only related to the OH detection difficulties or the accurately measured compound concentrations. Both of the latter should not be an issue nowadays! Secondary photochemistry of different sources is one of the issues that both techniques need to test and combat.

Major Concerns:

1. Why the authors didn't use the recommended rate coefficients from the two evaluation panels (IUPAC, NASA/JPL) for the reference reactions and they preferably, where exist? There are some issues with reproducing the quoted data in the tables. Also, in the section where they describe the criteria for reference reaction selections, they have fully omitted one of the most important criteria, which that is the reference reaction rate coefficient needs to be similar to the one under study, to increase measurement sensitivity. Please include. This way both axes range are similar and the concentration variations can be measured with similar precision. Also please include 1σ , not just σ in error analysis and describe if this includes systematic uncertainties (reference reaction rate coefficients are one of the major sources of that in relative rate determinations). In general, error analysis and references to that are vague. What is the meaning of 2σ levels on SAR? What are the major sources of errors (random and systematic) in their measurements?

2. Although the authors have used O₂, air (N₂/O₂), and N₂, as bath gases test measurements and interpretation analysis is incomplete. In general, it is common that when not enough/excess of O₂ is present in relative rate measurements, it is likely that the radicals are not efficiently scavenged and might initiate secondary chemistry, e.g., reactants – targeted or/and reference – regeneration or even chain chemistry that will result in rate coefficient underestimates or overestimates. Radicals react with O₂ pretty fast, e.g., typically in the order of 10^{-12} cm³ molecule⁻¹ s⁻¹ which is in the same range as the understudied reactions. In general, to test this, people run experiments at different O₂ levels to ensure that the rate coefficient is not altered. At pressures close to atmospheric pressure where ~150 Torr of O₂ is present, there is enough

of O₂ to scavenge the produced radicals, in most cases, which is not the case when the non-reactive N₂ is used as bath gas – there is always some small amount of O₂ even then. Although in the case of hydrogen metathesis, this does not always result in a problem, depending also on the rate coefficient of the studied reaction and the chemistry involved, it might be an issue for slower reactions that compete with radical oxidation. It would have been nice if the authors had experimentally demonstrated that and if not acknowledged this effect in the interpretation of their results.