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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Estimation of rate coefficients and branching ratios for gas-phase reactions of OH with aliphatic organic compounds for use in automated mechanism construction" *by* Michael E. Jenkin et al.

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This paper explores a new Structure-Activity Relationship (SAR) for H-atom abstraction by OH, and for OH-addition to a wide number of organic compounds. The work more than builds on previous studies. It is thorough and wide-reaching, and treats different classes of molecules consistently. The paper is presented clearly and logically, so it is easy to follow the arguments made in building up the SAR. I tried calculating a few rate constants for representative molecules in the supplement, and they worked!

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Discussion paper

One minor issue is that the increase in scope of the study comes with an increase in complexity of the SAR. There are now many more k's and F's than previously, and while the SAR is clearly going to be of value for automated mechanism generation, it might be a little daunting for every day users who want to quickly estimate a few rate constants.

For example, I noted around 10 different rate constant representations for OH + aldehydes in Table 4. This is presumably required to explain the observed differences in reactivity, but more fundamentally may represent a limit of the SAR concept where negative activation energies are involved (aldehydes, multifunctional oxygenates).

Maybe a little more discussion could be given to classes of compounds that are not represented very well, as a caveat to users. In addition to those mentioned above, I note that rate constants for alkanes with a lot of tertiary hydrogens are often overestimated, too. Steric effects coming into play? This also has ramifications for estimating the site of attack, too.

I have only minor comments on the manuscript, which is well prepared, and clear, as noted above.

Page 6, line 17. Regarding the inductive effect on OH + aldehydes: While outside the scope of this work, it is well known that the presence of halogens deactivates the aldehyde group strongly.

Section 4.1. Maybe explain explicitly that in contrast to the method of Kwok and Atkinson, this follows Peeters, in considering each end of the double bond separately (just to avoid any confusion). I like the Peeters approach, since it allows a better estimate of the potential product distribution if the alkoxy radicals formed have more than one decomposition pathway.

Table 14 (and text). These are described as "prompt" reactions of thermalized radicals, but I usually associate that term with excited (i.e. nascent) radicals, not stabilized ones.

P13 line 1: Should be Table 10.

Page 17, line 29-30: “formation of a resonant radical is not represented” is not totally clear. I assume you mean that the unpaired electron on the formyl group is perpendicular to the orbitals of the C=C bond and cannot overlap. Represented may not be the right word though.

Page 26, line 15. Noziere accent misplaced.

Page 29, line 6. Typo Tyndal should be Tyndall.

Table 4: Sixth entry has pentavalent carbon R = –CH(X)(Y)Z. Also, Arrhenius expression in Table 4 header has missing (or extra) parenthesis.

The representation of different functional groups in the tables of F(X) values is a little confusing at first. I take it that you are only showing the relevant substituents that affect the rate constant. So in Table 12, for example, under column X we see –C=CH-C=CHR and the third carbon has only 3 bonds. It took a little while to figure out the logic, but it works (I think).

Overall, this is a very impressive piece of work that will be of great value to the community.

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