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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Structure-activity relationship for the estimation of OH-oxidation rate constants of carbonyl compounds in the aqueous phase" *by* J. F. Doussin and A. Monod

Anonymous Referee #2

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General Comments

This paper presents a successful structure-activity relation (SAR) model that can be used to predict aqueous phase H-abstraction rate constants by OH radicals reacting with organic molecules. In this work, the model is extended to include ketones, aldehydes, and polyfunctional compounds with these functional groups, which are of great interest to atmospheric chemists. The original model, published in 2008, already included alcohols, acids, bases, and alkanes. The paper compiles hydration equilibrium constants (a valuable compilation for atmospheric chemists working on aqueous chemical processes) and hydroxyl radical H-abstraction rate constants that are all used for

model input. The inputs are used to solve for functional group terms for direct reaction with OH, and for the influence of functional groups on OH reaction rates with alpha- and beta-position neighboring groups. The usefulness of these terms for rate constant prediction is then tested, and the significance of the values derived for each term is discussed. The results suggest that the model can be used (with perhaps a factor of 2 accuracy) on other compounds where OH rate constants have not been measured yet. This paper is a significant contribution to efforts to predict OH rate constants.

Specific Comments

The model terms are used to predict OH rate constants, which are compared with the input data. As this calibration and testing activity on the same compounds seems like a circular process (albeit a necessary one), it is unsurprising that reasonable agreement is obtained, and also unsurprising that the model outperforms other SAR models on its native dataset. The authors should justify to what extent these comparisons between SAR models are fair, given the overlap or lack of overlap of data used to build and test each model.

Abstract / p. 15959 line 6: The authors should clarify what compounds they are including in the reported percentages of compounds where model predictions match measurements within a certain tolerance. In the abstract, they appear to be reporting a number based on results for all compounds used to develop the model (alcohols, acids, bases, alkanes, carbonyls, multifunctional), giving 58% of compounds matching within 20%. However, the more important result to include in the abstract is for the carbonyls and multifunctionals alone, the focus of this study. (On p. 15959 it is reported that only 41% of these compounds have predictions that match the measurement data within +/-20%.) It seems to me that the success of the previous version of the model is inflating the perceived success of the current extension when non-carbonyl compounds are included. It would be helpful to give these types of results for ketones + aldehydes and for polyfunctionals separately so that the reader can best judge the utility of the method.

p. 15959 line 15: Why is a limited diversity of structures a problem for model accuracy if the same structures used to develop the model are then used to validate it? Wouldn't this actually improve the model performance on these structures?

p. 15954 line 21: Cyclic descriptor terms are mentioned here, yet I can find no other mention or listing of such terms in the manuscript. Were these terms part of the previous model?

Figure 2: It appears that the rate constants for ketones and aldehydes are slightly but systematically underpredicted, while those for polyfunctionals are overpredicted. The manuscript should confirm and comment on these effects, if they are real.

The ease of interpretation of Figure 3 would be improved by adding labels for the categories included in each fit line – "ketones" and "aldehydes."

Technical Corrections

Abstract: "undertake" should be "undergo"

p. 15951 line 4: Eliminate "are" before "Not only"

p. 15955 last line: "otherwise mentioned" should be "unless mentioned"

p. 15956 line 6: add an article such as "a" before "pseudo"

p. 15959 line 23: no need to list four authors

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 15949, 2013.