

A Broad View of Structure-Activity Relationship Performance for Alkanes and Haloalkanes

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As a subset of the gas kinetic database, the alkanes and haloalkanes possess some remarkable properties. Considering that they each share a common reaction mechanism with atmospheric oxidants (i.e. hydrogen abstraction), this group displays a wide range of reactivity (e.g. 5 orders of magnitude in the OH dataset). Furthermore, because of long-standing concerns over their effects upon climate, the ozone layer and climate, they have attracted a large amount of interest since the 1970s. As a result, there is a wealth of information that is known about them in terms of their kinetics, spectroscopy, thermodynamics and many other properties besides.

This study takes a broad look at the types and performances of the structure-activity relationships (SARs) and linear free-energy relationships (LFERs) that are available to the alkanes and haloalkanes. Well-known approaches such as the group-additivity approaches of Atkinson and co-workers¹ and DeMore² are found to perform well. However, there are many other methods including the LFERs between oxidants (e.g. OH vs Cl); with ionization potential; bond-dissociation energy; and other thermochemical approaches. These estimation methods also demonstrate good predictive power.

As kinetic databases have improved, and as online machine-learning approaches, and rapid quantum chemical calculations have gotten better and become more accessible in recent years, this has allowed many of these methods to be augmented with additional computational data. Combining these developments with a new electrotopological approach that is unique to this study, a new level of coverage of the prediction-space of this family of compounds is achieved, and the possibility of an ensemble SAR prediction of rate coefficients is explored.

References

- [1] R. Atkinson, *International Journal of Chemical Kinetics*, **19** 799 (1987).
- [2] W.B. DeMore, *Journal of Physical Chemistry*, **100** 5813 (1996).