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Gas-phase kinetics and theoretical calculations to investigate the effects of substitution on the reactivity of unsaturated Volatile Organic Compounds

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INTRODUCTION

- Gas-phase electrophilic addition of OH represents the primary sink for alkenes in the atmosphere, where the degree and type of substitution strongly affects their chemical reactivity.
 - This leads to a diversity of behavior that has presented a challenge for structure-activity relationships (SARs).
- Here, we investigate and extend the potential of existing SARs to estimate temperature-dependent OH rate coefficients, $k(T)$, of a large range of alkenes under atmospheric conditions.

METHODOLOGY

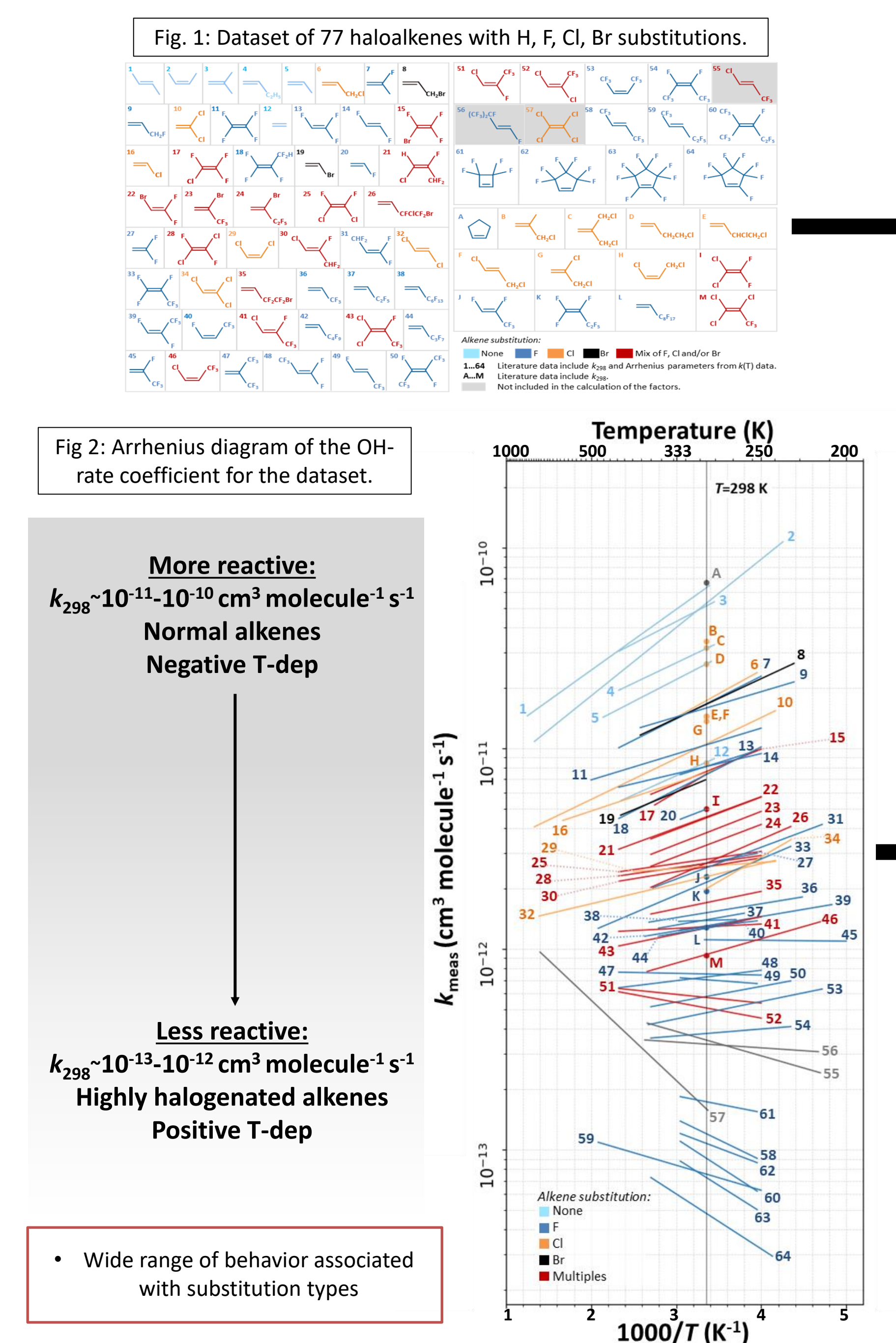
- We considered two different techniques: the group-additivity approach of Atkinson and co-workers^[1], and the recent method of Tokuhashi and co-workers^[2] to estimate k_{298} .
- The latter was found to make superior predictions for halogenated olefins. This SAR was extended to include more species, and to predict temperature dependences.

MAIN OBJECTIVE

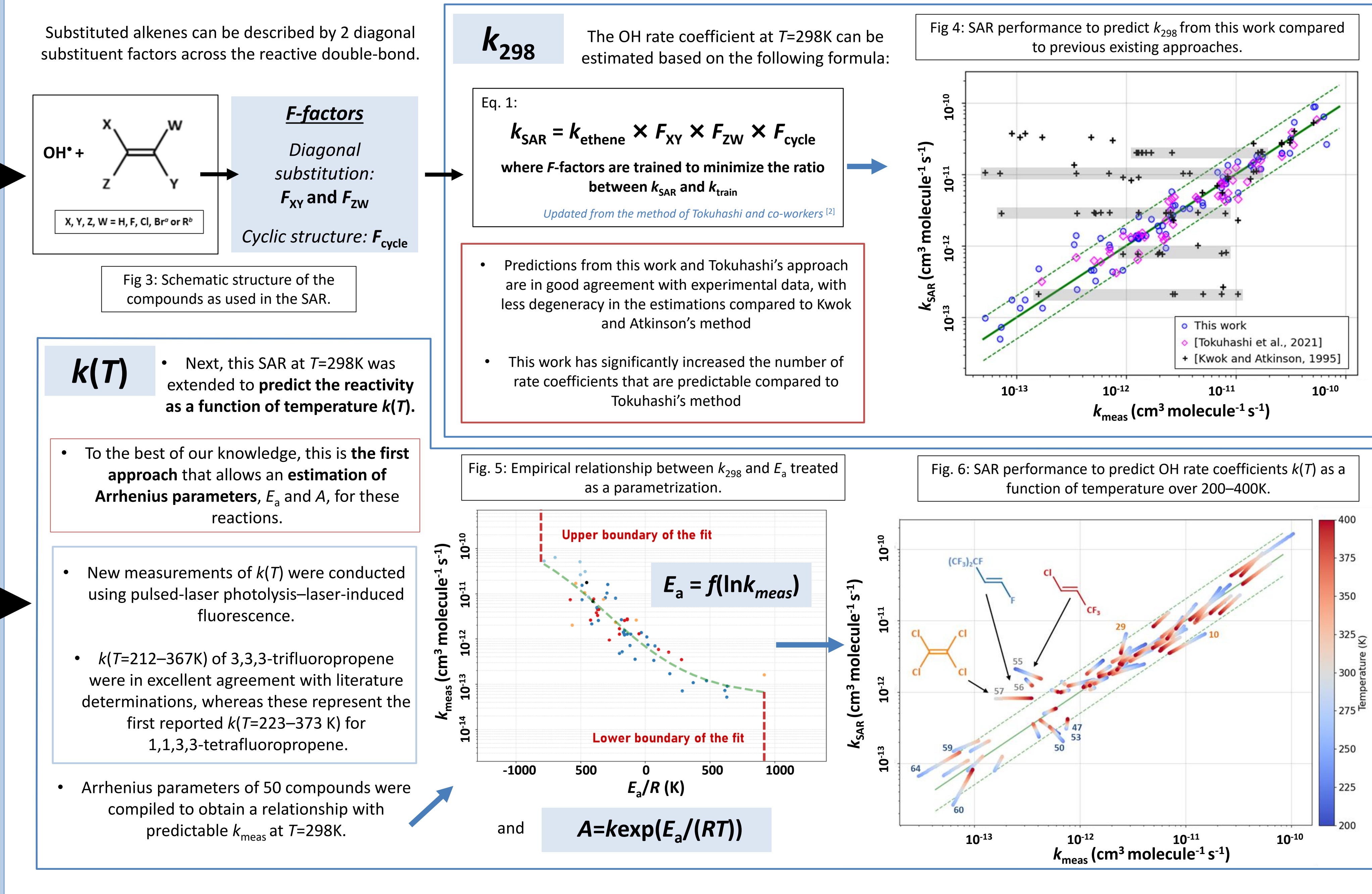
Build a hybrid easy-to-use screening tool, usable with or without experimental data, for assessing the environmental impact of these compounds before they reach the mass-production phase.

Previous work [3]

(1) Experimental data [4]



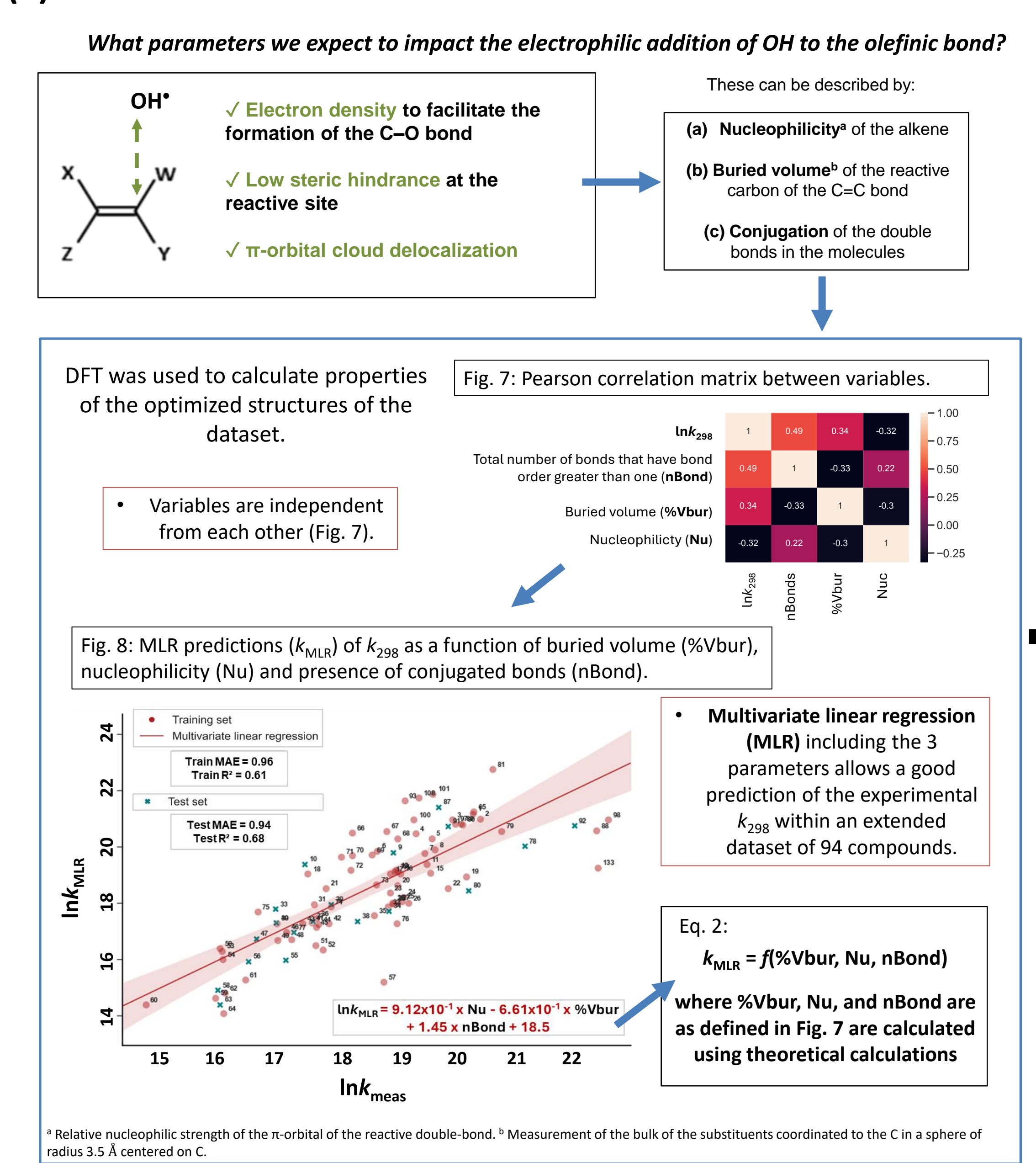
(2) Structure-activity relationship (SAR)



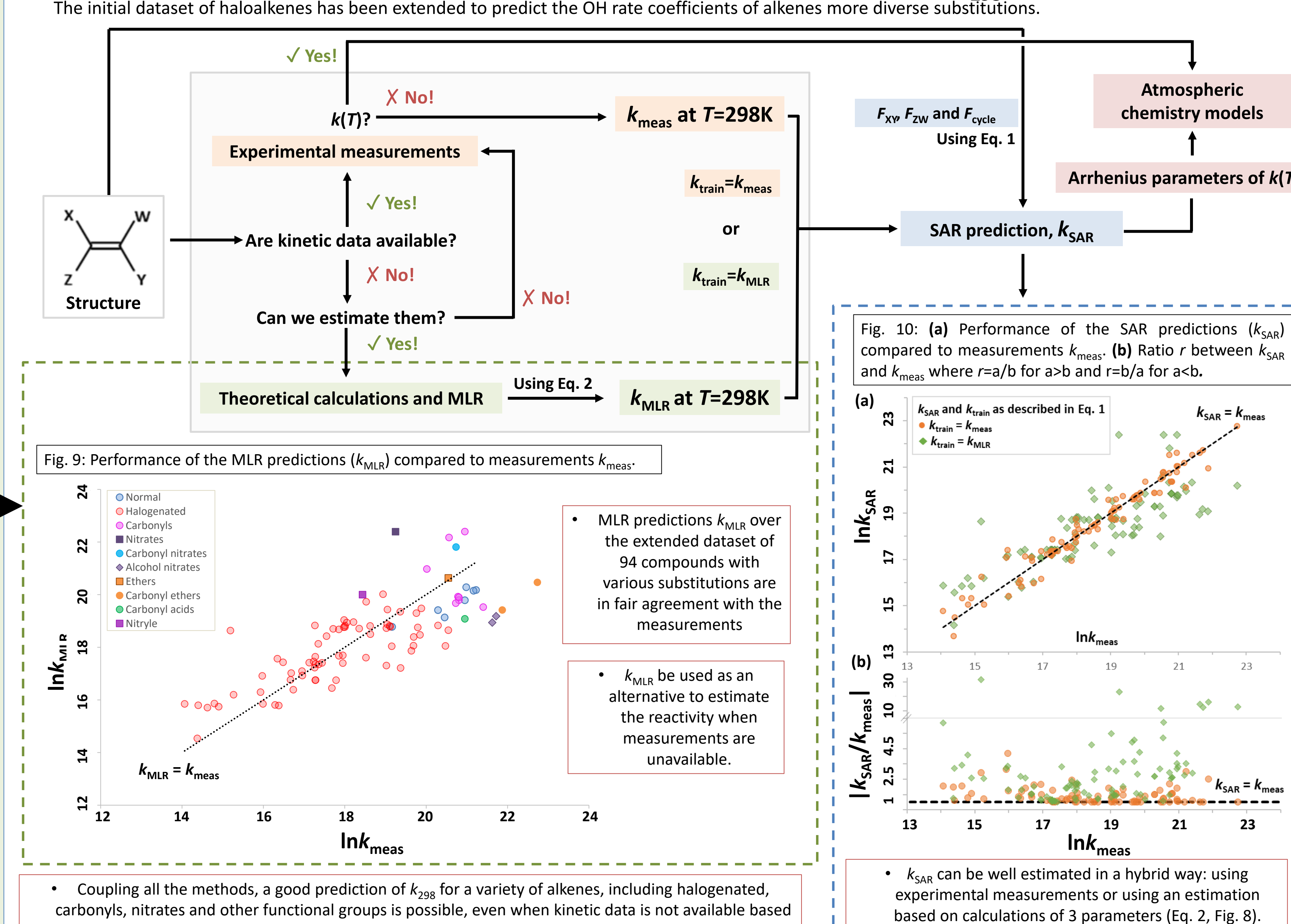
How to refine the SAR and include a larger variety of predictable compounds?

Work in progress

(3) Theoretical calculations conducted at CSU in collaboration with the research group of Dr. R. Paton.



(4) Combining measurements, SAR and theoretical calculations to predict k_{298} for more species.



CONCLUSION

- Using only the structure, we are able to predict temperature-dependent OH rate coefficients for 77 haloalkenes over $T=200\text{--}400\text{K}$
- Good SAR performance to predict k_{298} and $k(T)$ compared to previous existing approaches^{[1],[2]} and experimental data
- First method to predict Arrhenius parameters of the OH-reaction rate coefficient with haloalkenes

IN PROGRESS

- SAR prediction at $T=298\text{K}$ has been extended to more types of substitutions (with 17 additional compounds) with new functional groups ($=\text{O}$, $-\text{O}-$, $-\text{OH}$, $-\text{ONO}_2$, $-(=\text{O})\text{OH}$, or N)
- Development of a hybrid tool that combines SAR, theoretical calculations and experimental measurements to predict k_{298} only based on the structure of the alkene

PERSPECTIVES

- Extend this tool to predict Arrhenius parameters
- Include a larger diversity of compounds relevant for atmospheric chemistry

References

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