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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

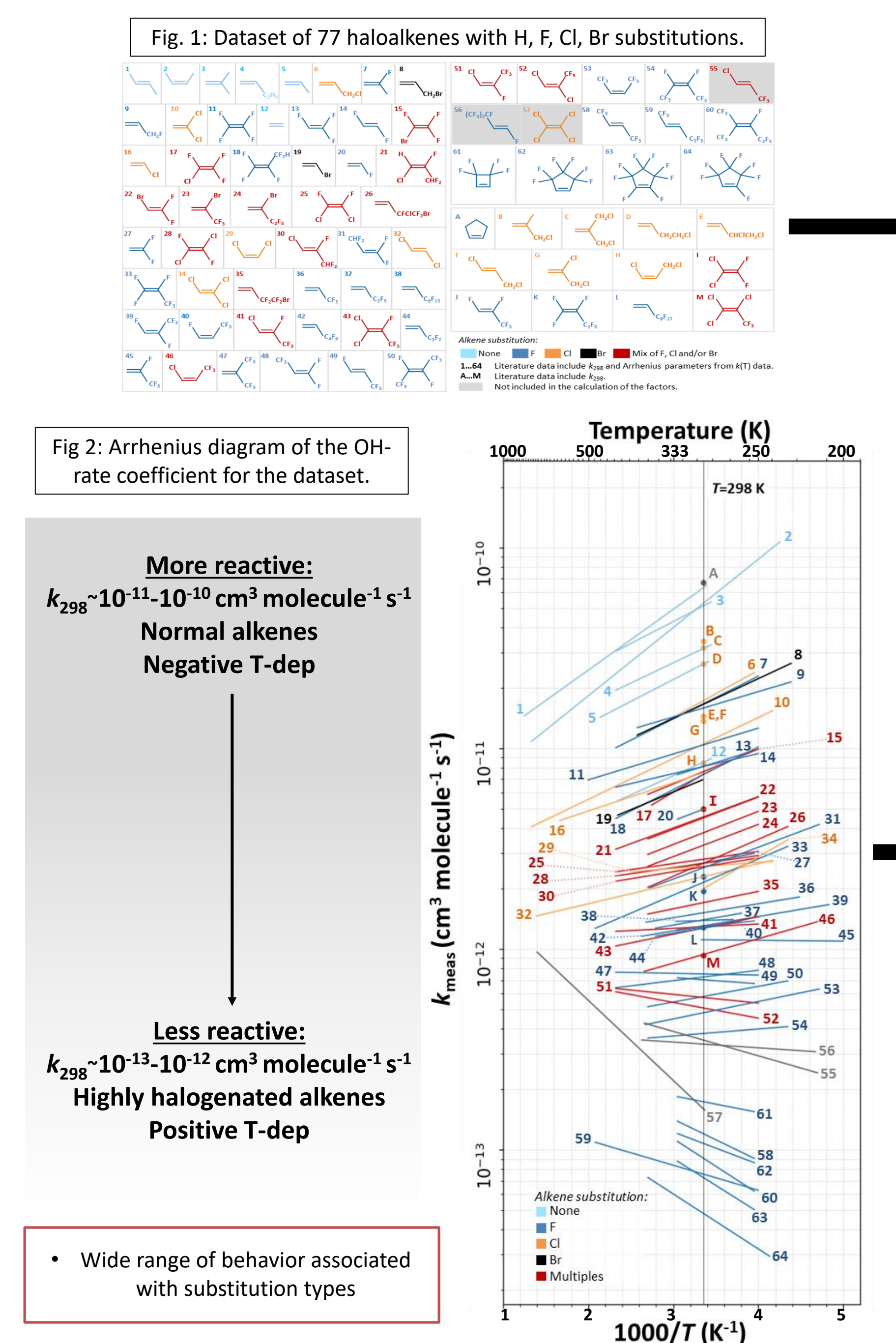
- We considered two different techniques: the group-additivity approach of Atkinson and co-workers^[1], and the recent method of Tokuhashi and co-workers^[2] to estimate k_{298} .
- The latter was found to make superior predictions for halogenated olefins. This SAR was extended to include more species,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

Substituted alkenes can be described by 2 diagonal substituent factors across the reactive double-bond.

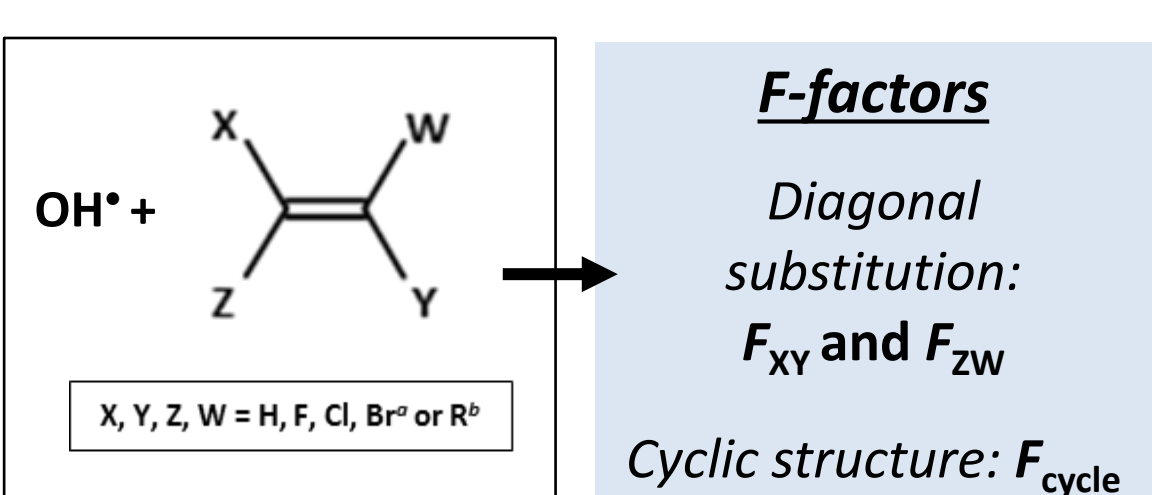


Fig 3: Schematic structure of the compounds as used in the SAR.

$k(T)$

Next, this SAR at $T=298\text{K}$ was extended to predict the reactivity as a function of temperature $k(T)$.

- To the best of our knowledge, this is the first approach that allows an estimation of Arrhenius parameters, E_a and A , for these reactions.

- New measurements of $k(T)$ were conducted using pulsed-laser photolysis-laser-induced fluorescence.
- $k(T=212-367\text{K})$ of 3,3,3-trifluoropropene were in excellent agreement with literature determinations, whereas these represent the first reported $k(T=223-373\text{K})$ for 1,1,3,3-tetrafluoropropene.

- Arrhenius parameters of 50 compounds were compiled to obtain a relationship with predictable k_{meas} at $T=298\text{K}$.

k_{298}

The OH rate coefficient at $T=298\text{K}$ can be estimated based on the following formula:

Eq. 1:

$$k_{\text{SAR}} = k_{\text{ethene}} \times F_{XY} \times F_{ZW} \times F_{\text{cycle}}$$

where F -factors are trained to minimize the ratio between k_{SAR} and k_{train}

Updated from the method of Tokuhashi and co-workers^[2]

- Predictions from this work and Tokuhashi's approach are in good agreement with experimental data, with less degeneracy in the estimations compared to Kwok and Atkinson's method
- This work has significantly increased the number of rate coefficients that are predictable compared to Tokuhashi's method

Fig 4: SAR performance to predict k_{298} from this work compared to previous existing approaches.

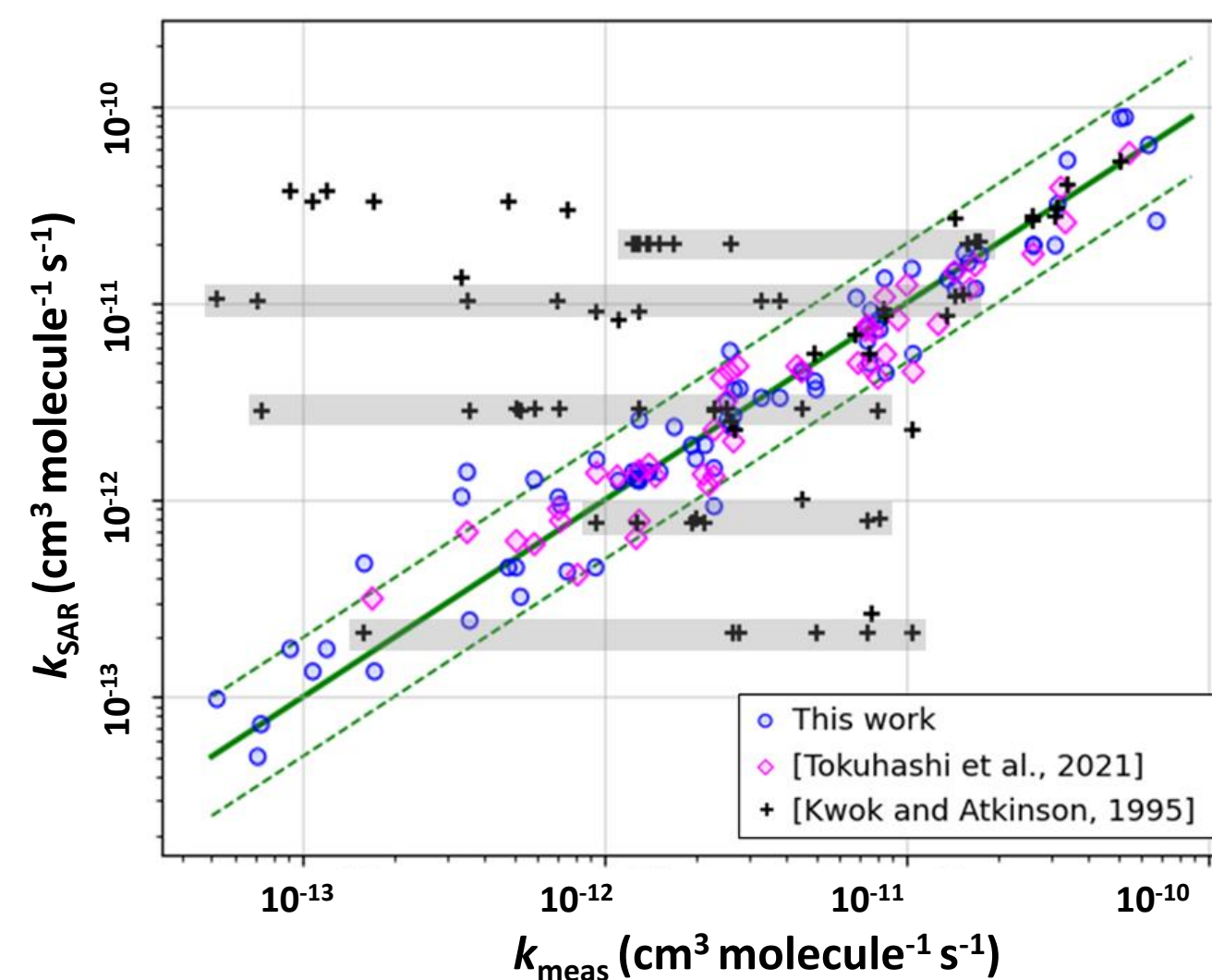


Fig. 5: Empirical relationship between k_{298} and E_a treated as a parametrization.

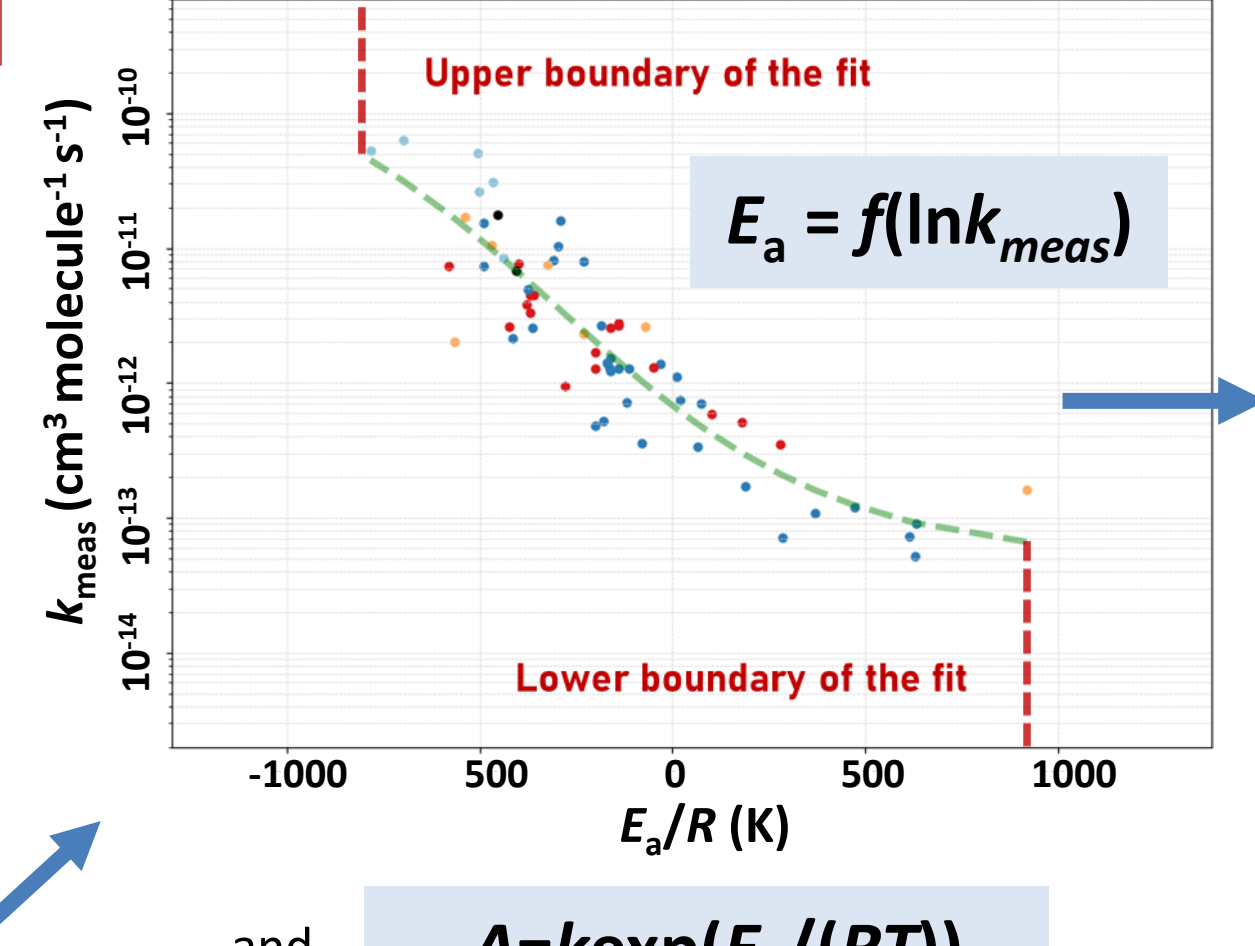
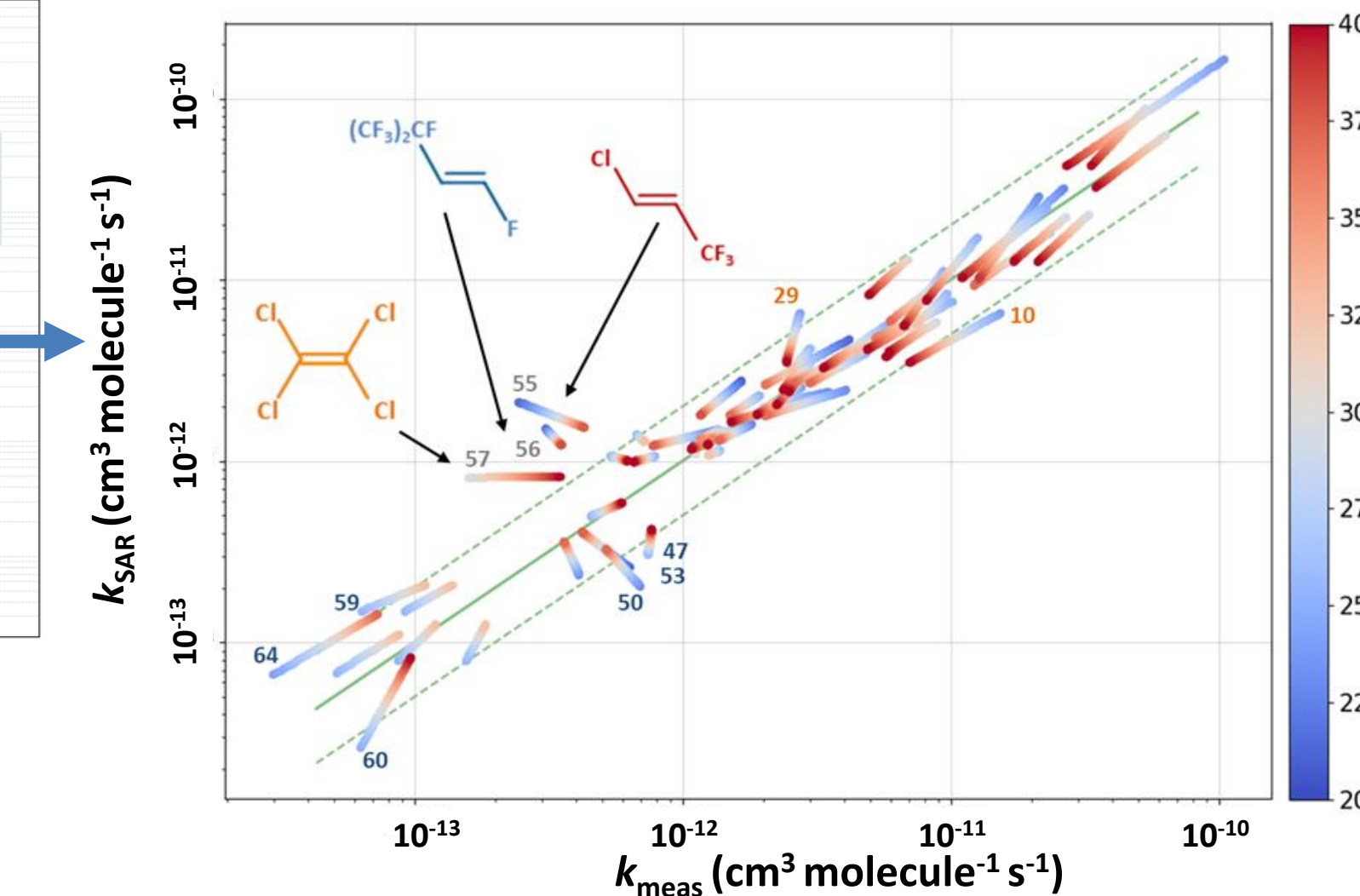


Fig. 6: SAR performance to predict OH rate coefficients $k(T)$ as a function of temperature over 200-400K.

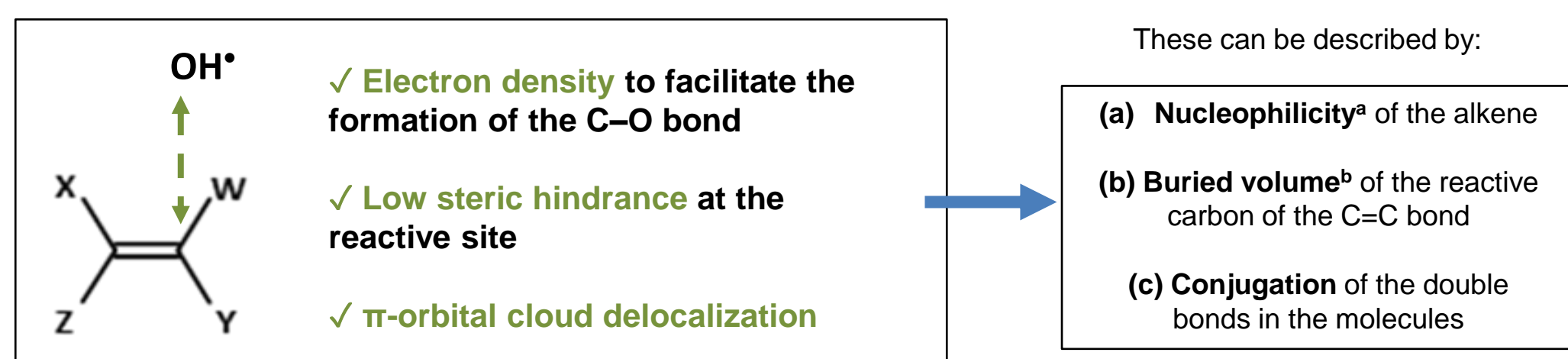


How to refine the SAR and include a larger variety of predictable compounds?

Work in progress

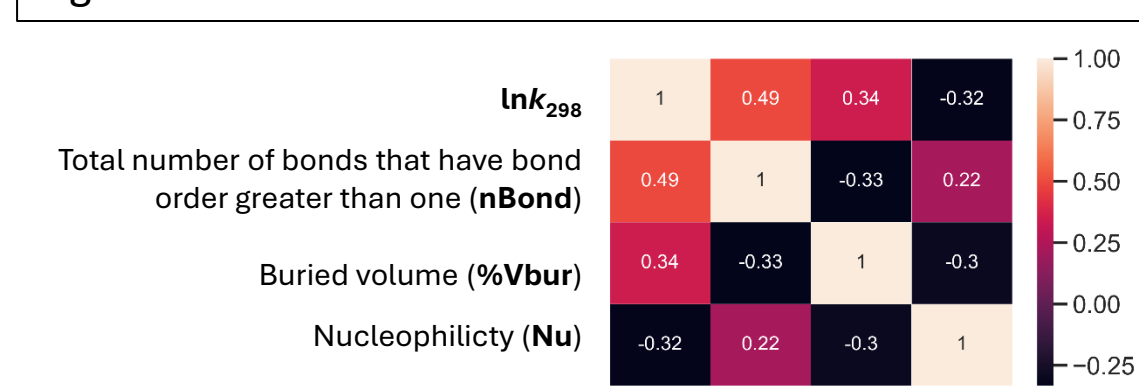
(3) Theoretical calculations conducted at CSU in collaboration with the research group of Dr. R. Paton.

What parameters we expect to impact the electrophilic addition of OH to the olefinic bond?



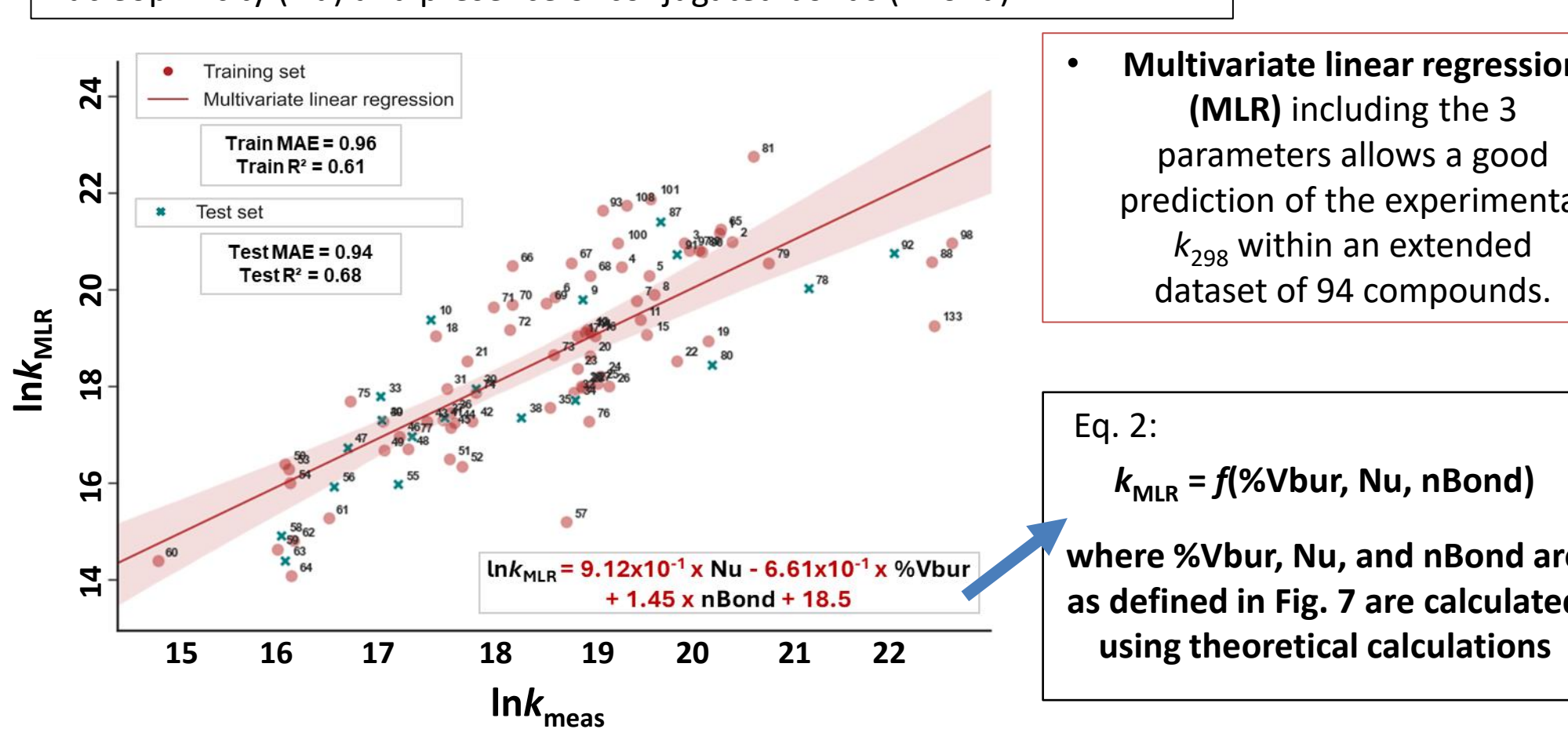
DFT was used to calculate properties of the optimized structures of the dataset.

Fig. 7: Pearson correlation matrix between variables.



- Variables are independent from each other (Fig. 7).

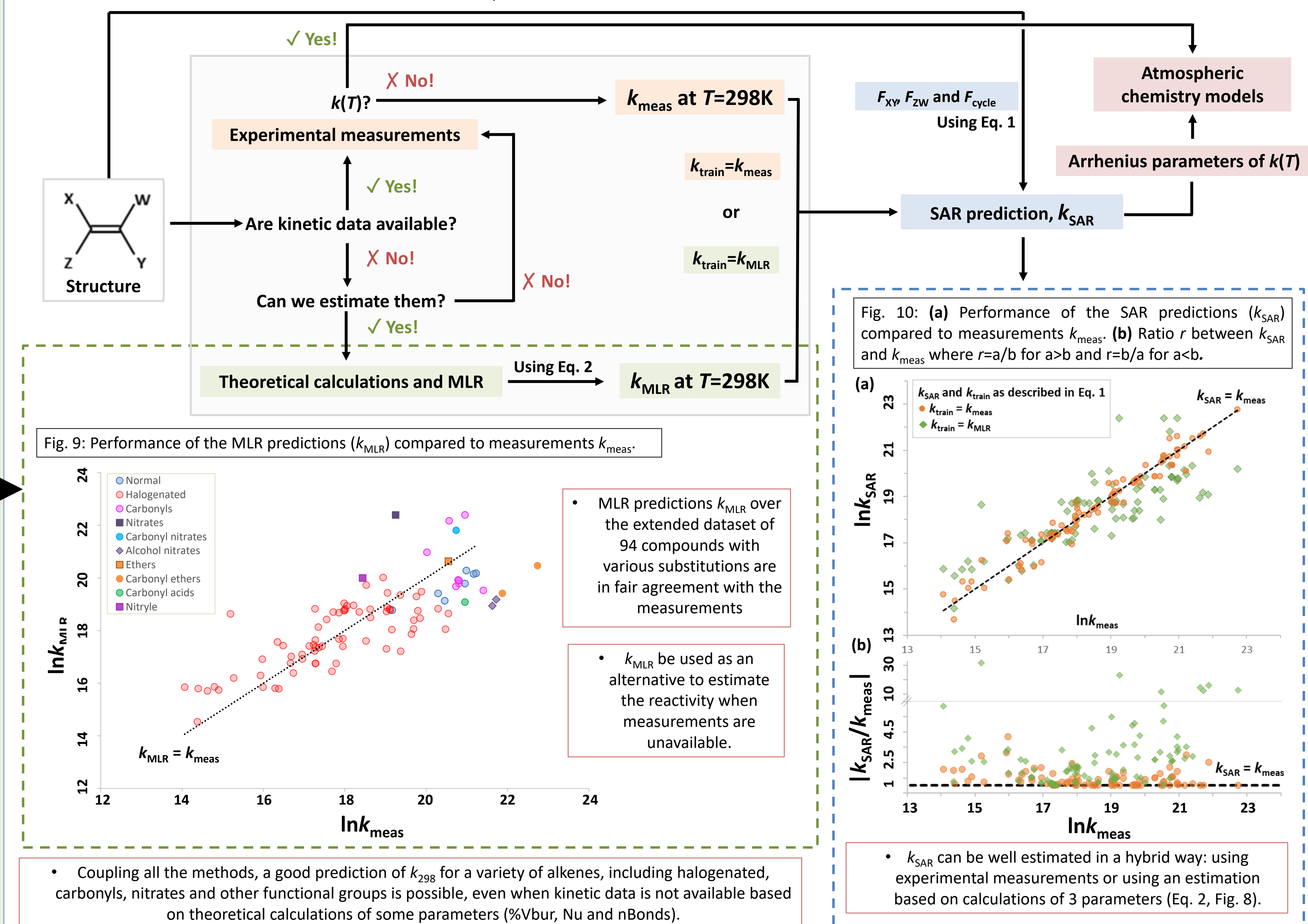
Fig. 8: MLR predictions (k_{MLR}) of k_{298} as a function of buried volume (%Vbur), nucleophilicity (Nu) and presence of conjugated bonds (nBond).



^a Relative nucleophilic strength of the π -orbital of the reactive double-bond. ^b Measurement of the bulk of the substituents coordinated to the C in a sphere of radius 3.5 Å centered on C.

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

The initial dataset of haloalkenes has been extended to predict the OH rate coefficients of alkenes more diverse substitutions.



CONCLUSION

- Using only the structure, we are able to predict temperature-dependent OH rate coefficients for 77 haloalkenes over $T=200-400\text{K}$
- 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 ($=O$, $-O-$, $-OH$, $-ONO_2$, $-(=O)OH$, or $\equiv N$)
- 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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