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

Lisa Michelat, Wahid Mellouki, Akkihebbal R. Ravishankara, Véronique Daële, Max R Mcgillen

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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

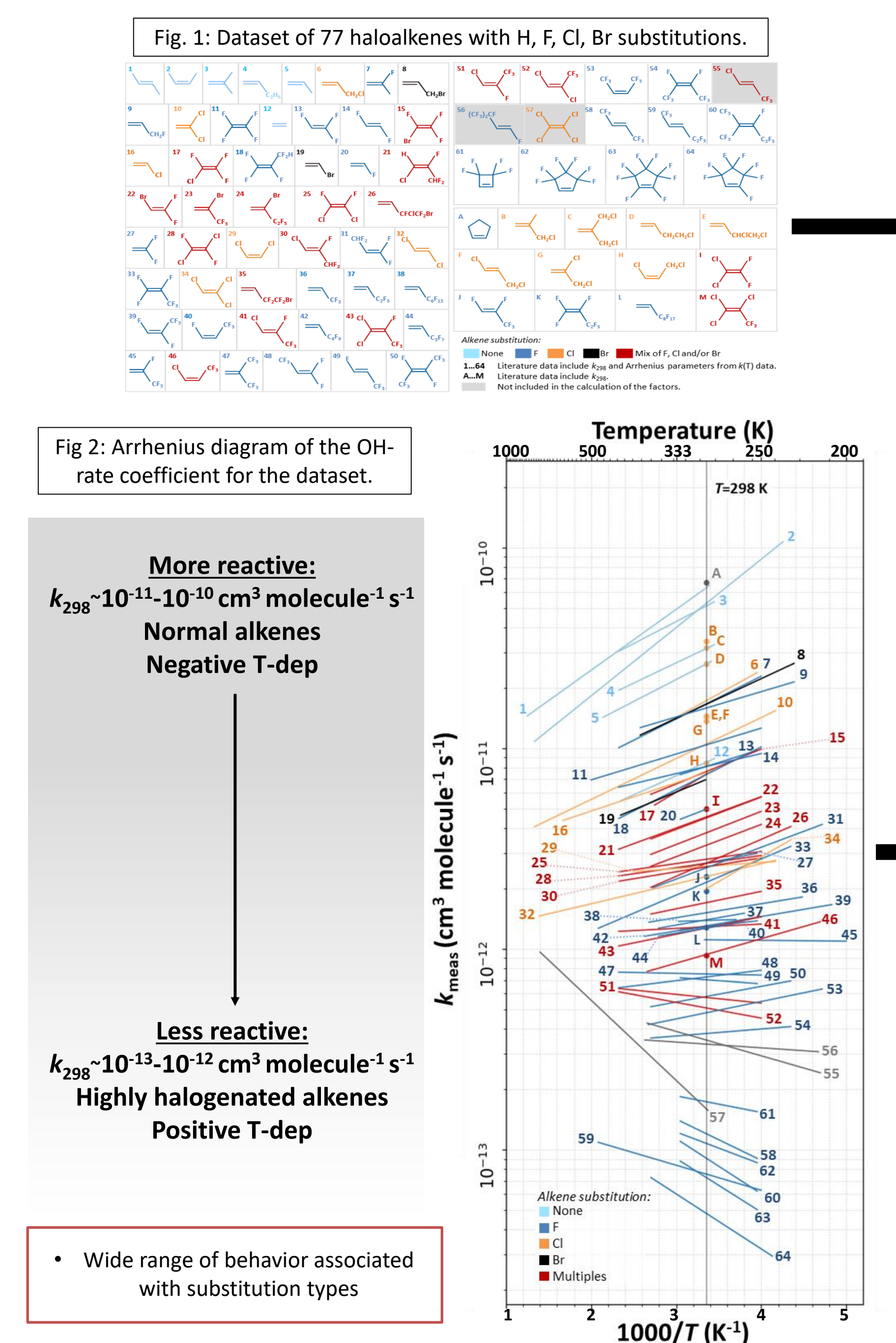
- We considered two different techniques: the group-additivity approach of Atkinson and co-workers<sup>[1]</sup>, and the recent method of Tokuhashi and co-workers<sup>[2]</sup> to estimate  $k_{298}$ .
- The latter was found to make superior predictions for halogenated olefins. This SAR was extended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

## MAIN OBJECTIVE

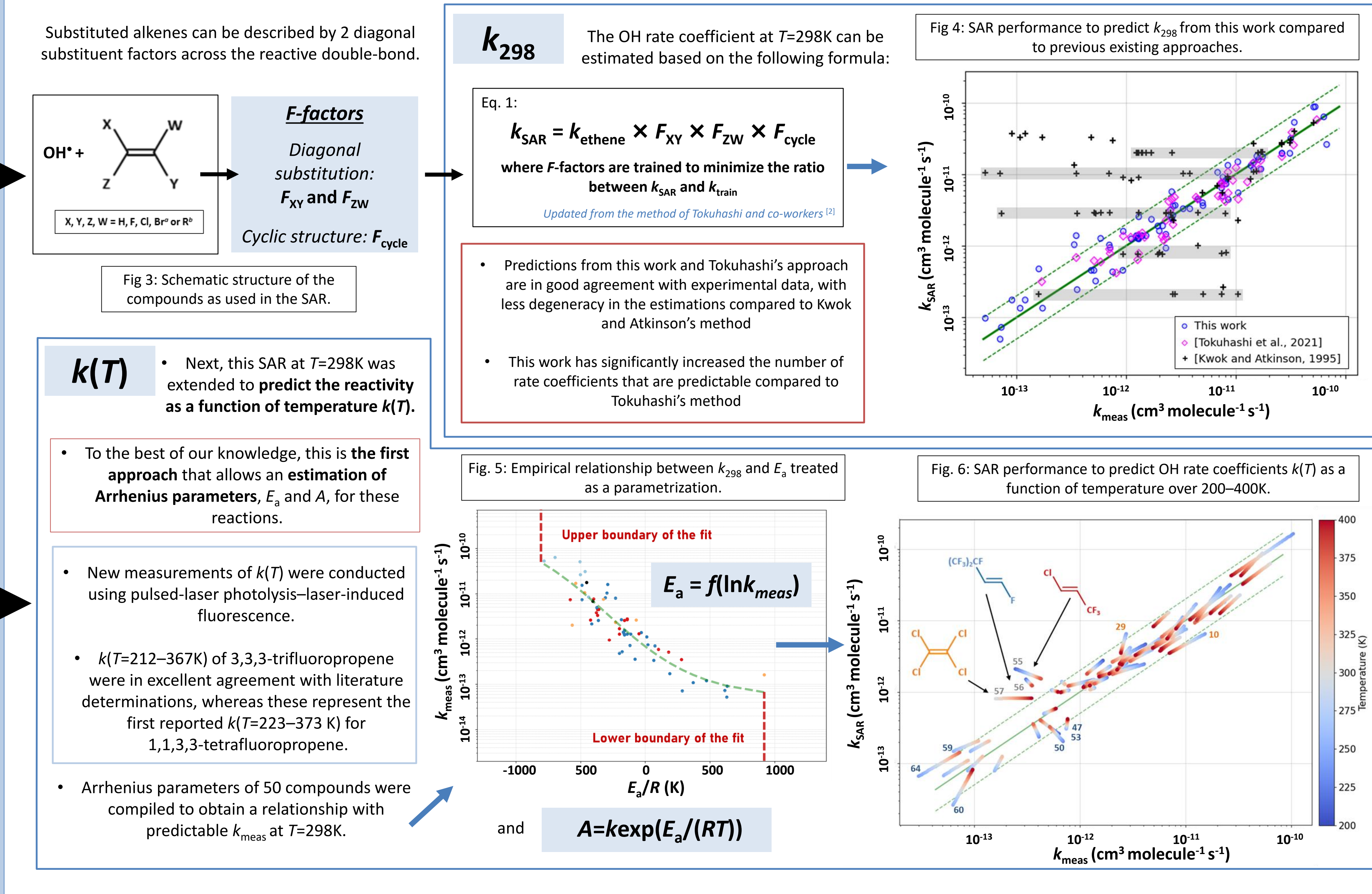
Build a hybrid easy-to-use screening tool, usable with or without experimental data, for assessing the environmental impact of these compounds before they reach the mass-production phase.

## Previous work [3]

### (1) Experimental data [4]



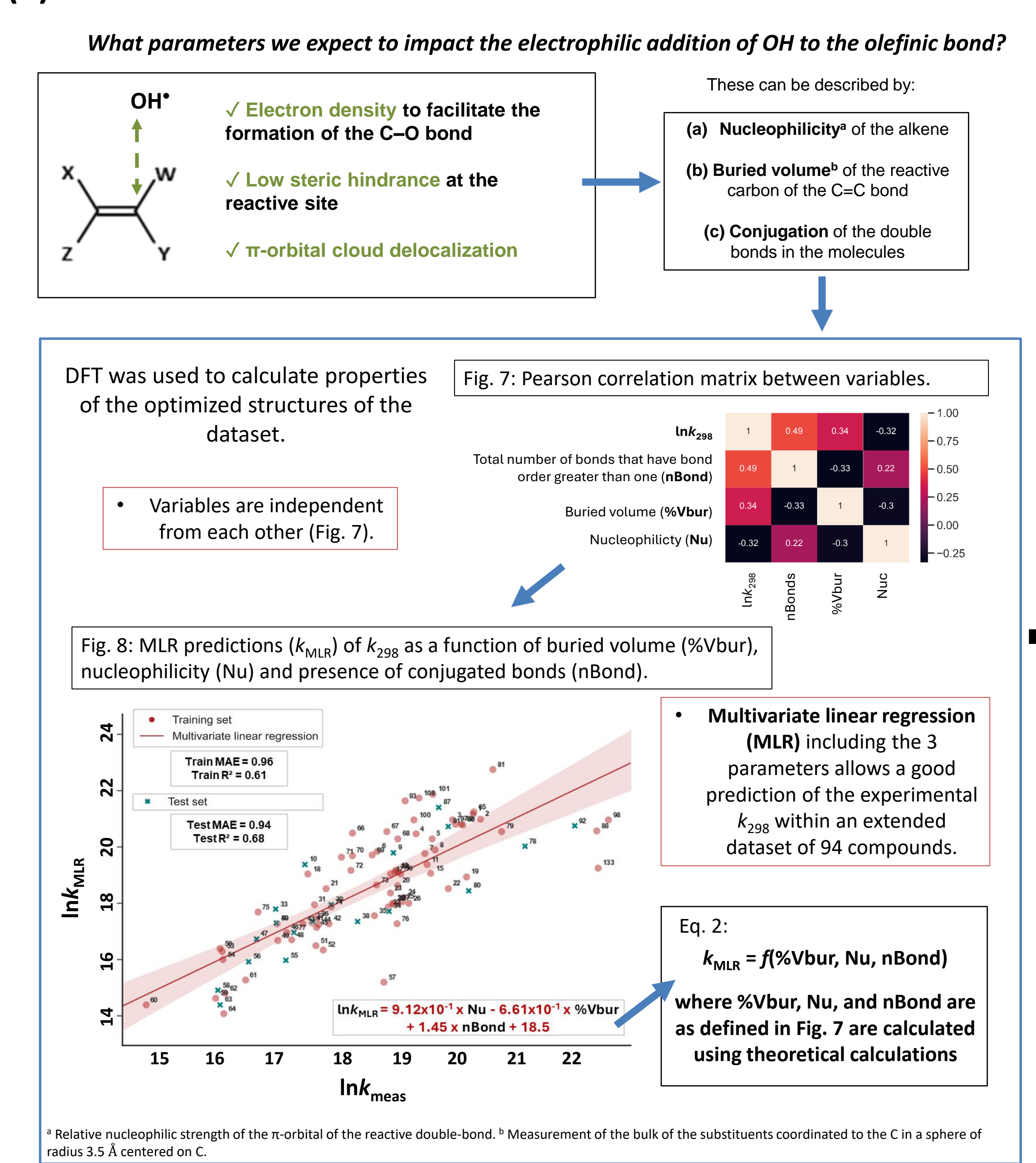
### (2) Structure-activity relationship (SAR)



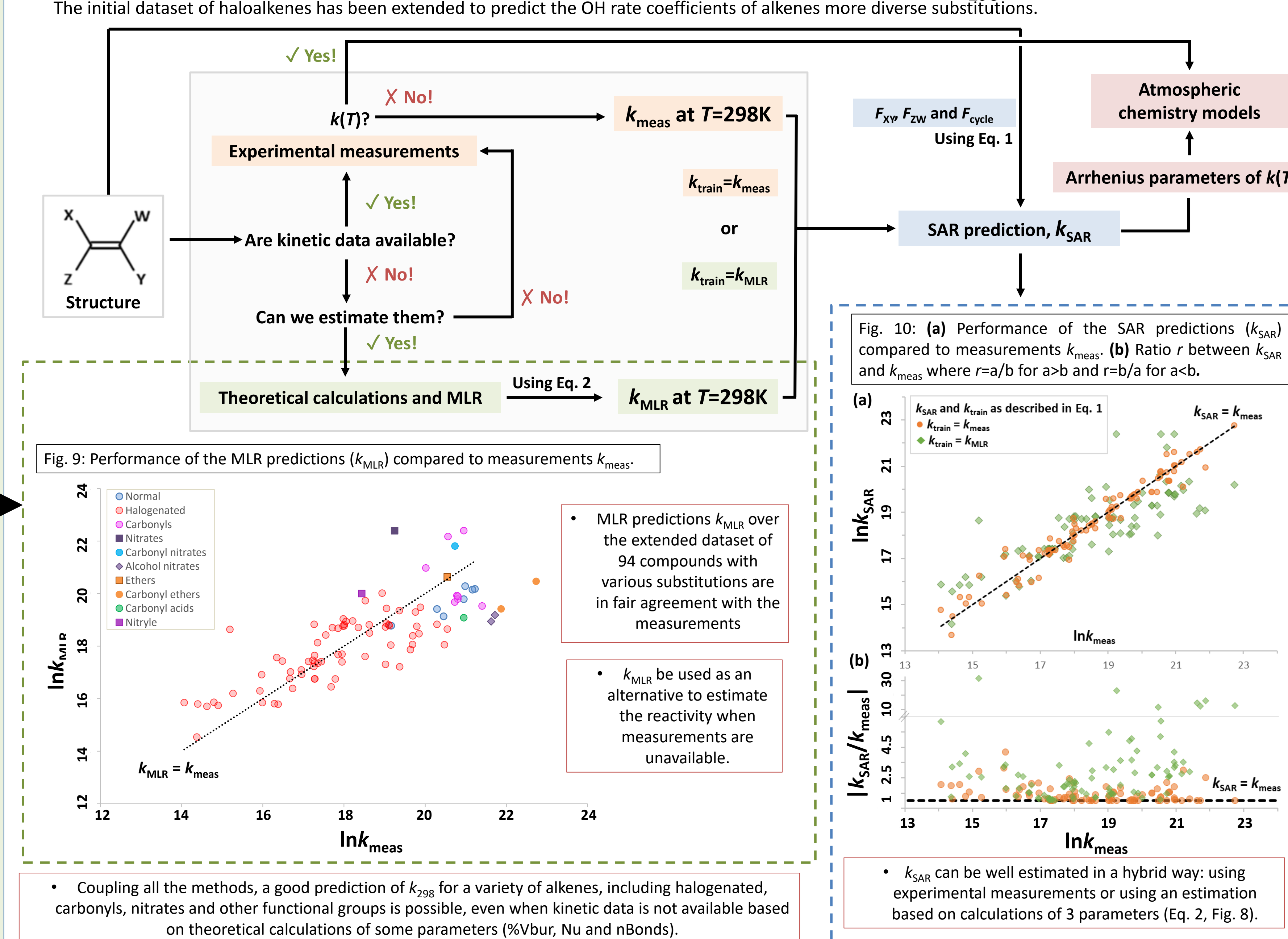
## How to refine the SAR and include a larger variety of predictable compounds?

## 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  $T=200-400\text{K}$
- Good SAR performance to predict  $k_{298}$  and  $k(T)$  compared to previous existing approaches<sup>[1],[2]</sup> 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  $\text{N}$ )
- 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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