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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

1. 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}.
2. 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]

Fig. 1: Dataset of 77 haloalkenes with H, F, Cl, Br substitutions.

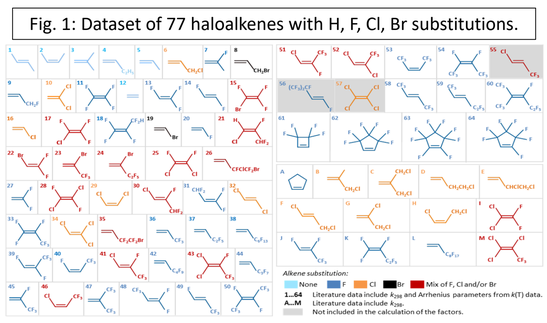
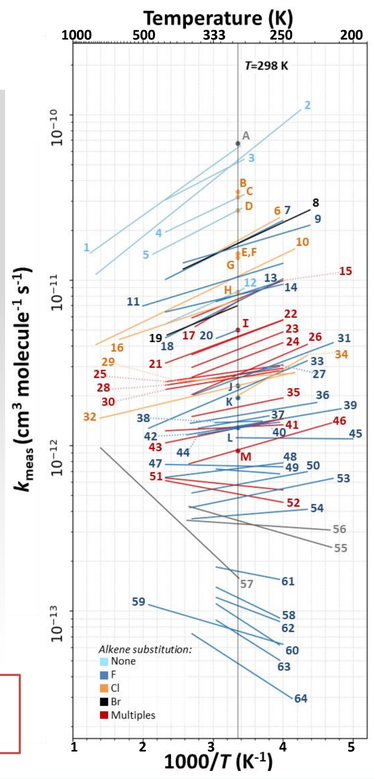


Fig 2: Arrhenius diagram of the OH-rate coefficient for the dataset.



More reactive:
k_{298}~10^{-11}-10^{-10} cm³ molecule⁻¹ s⁻¹
Normal alkenes
Negative T-dep

Less reactive:
k_{298}~10^{-13}-10^{-12} cm³ molecule⁻¹ s⁻¹
Highly halogenated alkenes
Positive T-dep

- Wide range of behavior associated with substitution types

(2) Structure-activity relationship (SAR)

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

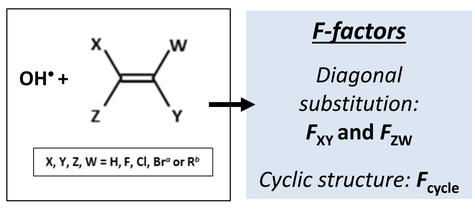


Fig 3: Schematic structure of the compounds as used in the SAR.

k_{298}

The OH rate coefficient at T=298K can be estimated based on the following formula:

Eq. 1:

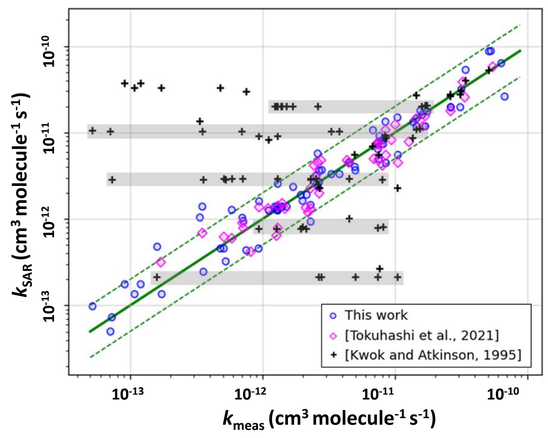
$$k_{SAR} = k_{ethene} \times F_{XY} \times F_{ZW} \times F_{cycle}$$

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

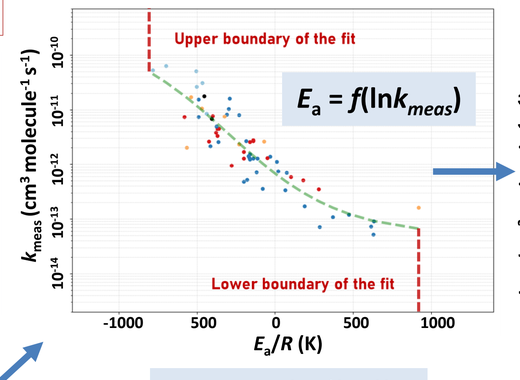
Fig 4: SAR performance to predict k_{298} from this work compared to previous existing approaches.



$k(T)$

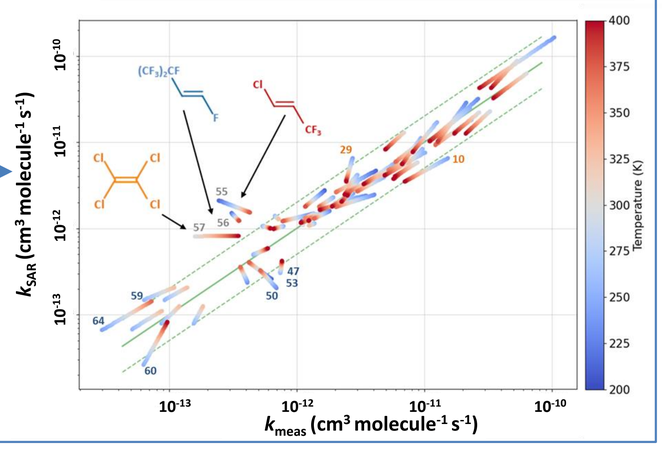
- Next, this SAR at T=298K was extended to **predict the reactivity as a function of temperature $k(T)$.**
- To the best of our knowledge, this is **the first approach** that allows an **estimation of Arrhenius parameters**, E_a and A, for these reactions.
- New measurements of $k(T)$ were conducted using pulsed-laser photolysis–laser-induced fluorescence.
- $k(T$=212–367K) of 3,3,3-trifluoropropene were in excellent agreement with literature determinations, whereas these represent the first reported $k(T$=223–373 K) for 1,1,3,3-tetrafluoropropene.
- Arrhenius parameters of 50 compounds were compiled to obtain a relationship with predictable k_{meas} at T=298K.

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



and $A = k\exp(E_a/(RT))$

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



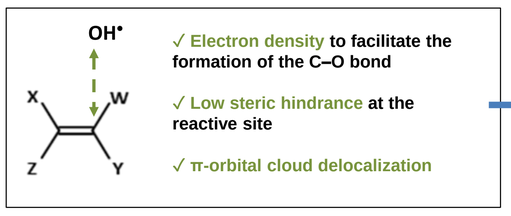
How to refine the SAR and include a larger variety of predictable compounds?

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?



✓ Electron density to facilitate the formation of the C–O bond

✓ Low steric hindrance at the reactive site

✓ π-orbital cloud delocalization

These can be described by:

(a) **Nucleophilicity**[a] of the alkene

(b) **Buried volume**[b] of the reactive carbon of the C=C bond

(c) **Conjugation** of the double bonds in the molecules

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

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

Fig. 7: Pearson correlation matrix between variables.

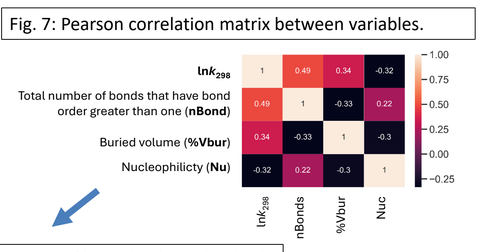
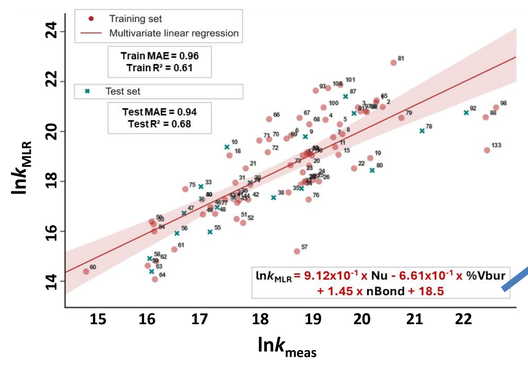


Fig. 8: MLR predictions (k_{MLR}) of k_{298} as a function of buried volume (%Vbur), nucleophilicity (Nu) and presence of conjugated bonds (nBond).



- **Multivariate linear regression (MLR)** including the 3 parameters allows a good prediction of the experimental k_{298} within an extended dataset of 94 compounds.

Eq. 2:

$$k_{MLR} = f(\%Vbur, Nu, nBond)$$

where %Vbur, Nu, and nBond are as defined in Fig. 7 are calculated using theoretical calculations

[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.

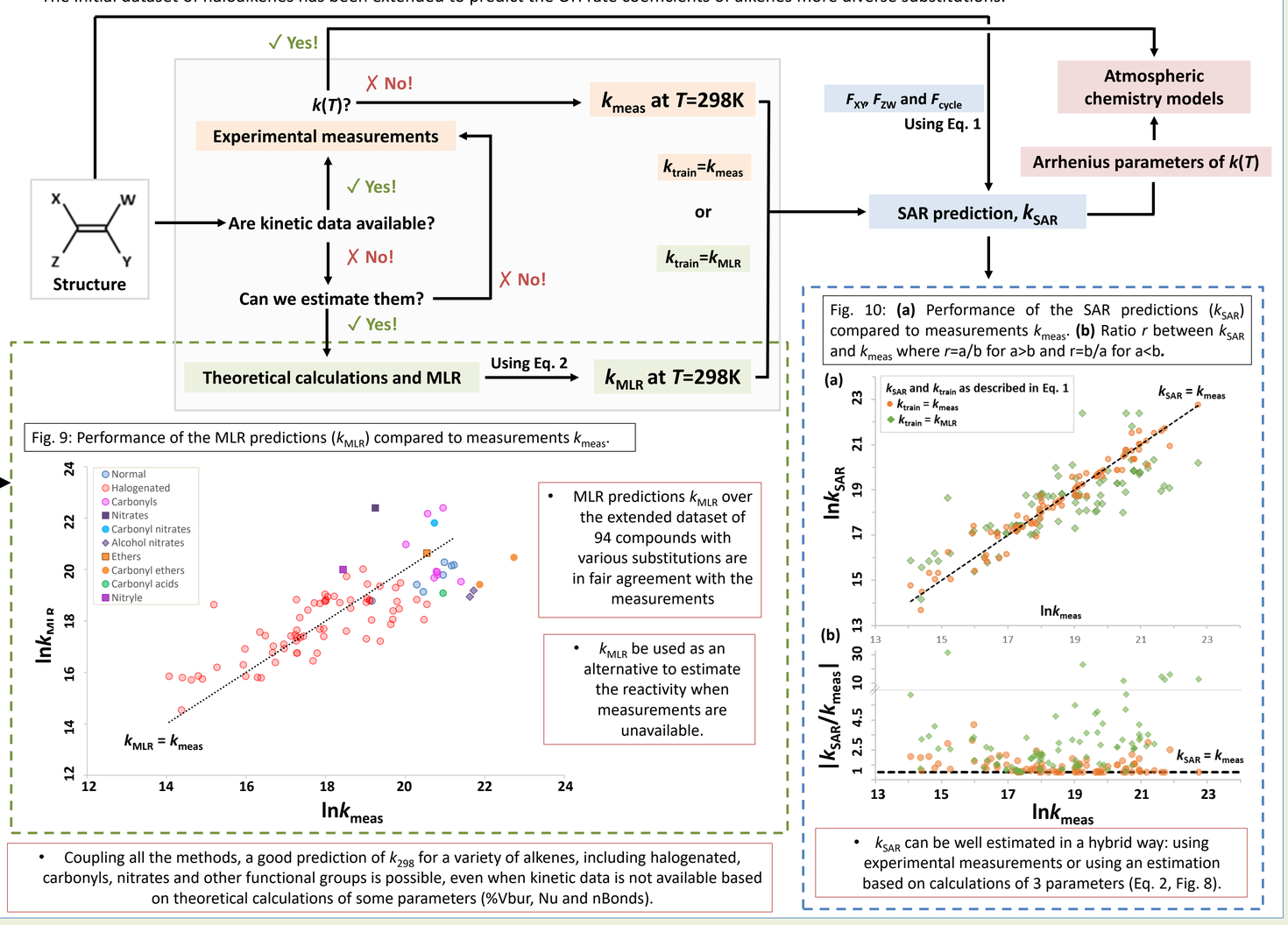


Fig. 9: Performance of the MLR predictions (k_{MLR}) compared to measurements k_{meas}.

- MLR predictions k_{MLR} over the extended dataset of 94 compounds with various substitutions are in fair agreement with the measurements
- k_{MLR} be used as an alternative to estimate the reactivity when measurements are unavailable.

Fig. 10: **(a)** Performance of the SAR predictions (k_{SAR}) compared to measurements k_{meas}. **(b)** Ratio r between k_{SAR} and k_{meas} where r=a/b for a>b and r=b/a for a<b.

- k_{SAR} can be well estimated in a hybrid way: using experimental measurements or using an estimation based on calculations of 3 parameters (Eq. 2, Fig. 8).

- Coupling all the methods, a good prediction of k_{298} for a variety of alkenes, including halogenated, carbonyls, nitrates and other functional groups is possible, even when kinetic data is not available based on theoretical calculations of some parameters (%Vbur, Nu and nBonds).

CONCLUSION

✓ Using only the strucure, we are able to predict temperature-dependent OH rate coefficients for 77 haloalkenes over T=200-400K
✓ 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=298K has been extended to more types of substitutions (with 17 additional compounds) with new functional groups (=O, -O-, -OH, $-ONO_2$,-(=O)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

[1] R. Atkinson. Estimation of gas phase hydroxyl radical rate constants for organic chemicals. *Environ. Toxicol. Chem. Int. J.*, 7, 435–442 (1988).
[2] K. Tokuhashi, K. Takizawa, S. Kondo. Rate constants for reactions of OH radicals with (Z)CF3CCl= CHCl, CHF2CF= CF2, (E) CF3CH= CHF, (Z) CF3CH= CHF, CH3CF= CH2, and CH2FCH= CH2. *Atmos. Environ.*, 255, 118428 (2021).
[3] L. Michelat, A. Mellouki, A.R. Ravishankara, H. El Othmani, V.C. Papadimitriou, V. Daële, and M.R. McGillen. Temperature dependent structure-activity relationship of OH + haloalkene rate coefficients under atmospheric conditions and supporting measurements. *ACS Earth Space Chem*. [in prep.] (2022).
[4] M. R. McGillen, W. P. Carter, A. Mellouki, J. J. Orlando, B. Picquet-Varrault, T.J. Wallington. Database for the Kinetics of the Gas-Phase Atmospheric Reactions of Organic Compounds. *Earth Syst. Sci. Dat*, 12 (2), 1203–1216 (2020).