A Computational Approach for Predicting Reaction Rate Coefficients of Organic Molecules in Atmospheric Hydrogen Abstraction Reactions

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INTRODUCTION

Approximate reaction rate coefficients can be found using structure activity relationships (SARs) for gas phase hydrogen atom abstraction reactions. However, this method has several limitations because it was first trained to evaluate specific classes of molecules and may perform poorly when applied outside its training domain. While SAR predictions showed good agreement for simple alkanes and small oxygenated compounds, larger deviations were observed for fluorinated hydrocarbons and ethers, particularly highly fluorinated species. This study seeks to implement a new method of determining the reaction rate coefficents of several molecules in the atmosphere using computation chemistry methods. This new technique considers the well-established relationship between hydrogen abstraction rates and C–H bond dissociation enthalpy (BDE), a property that can be calculated efficiently and accurately using Gaussian. Utilizing this quantum chemistry based approach allows for generalizability across structurally diverse classes of atmospheric compounds.

RESULTS

Both graphs show an overall positive correlation with measured values however, distinct differences emerge across chemical classes. Compared to Figure 1, Figure 2 exhibits reduced scatter and closer agreement with measured values for alkanes and ethers. In contrast, agreement decreases for certain functional groups, particularly ketones and nitriles. The traditional structure activity relationship method tends to overestimate reaction rate coefficients for several compound classes, including aldehydes and alcohols, whereas the bond dissociation energy based approach more frequently underestimates these rates. For the BDE method, many fluorinated hydrocarbons had predicted values that were within ±0.2 log units of measured rates. These systematic differences highlight how each method responds differently to functional group effects and molecular structure.

REFRENCES

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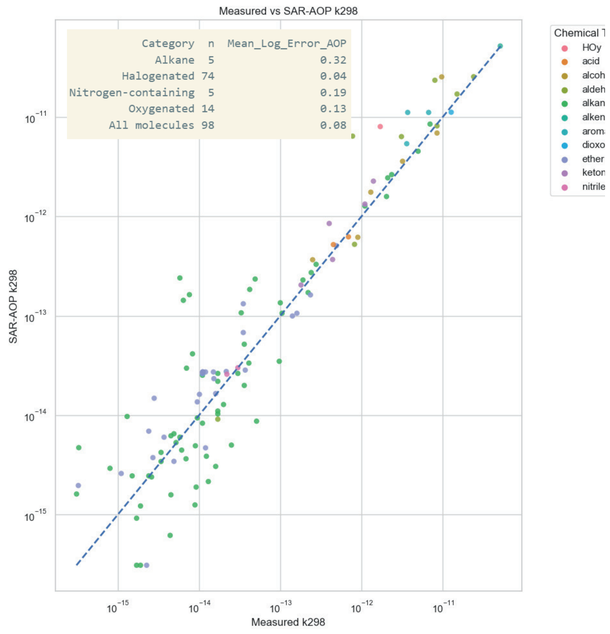

Figure 1- Measured reaction rate coefficients vs reaction rate coefficients found using the traditional SAR method

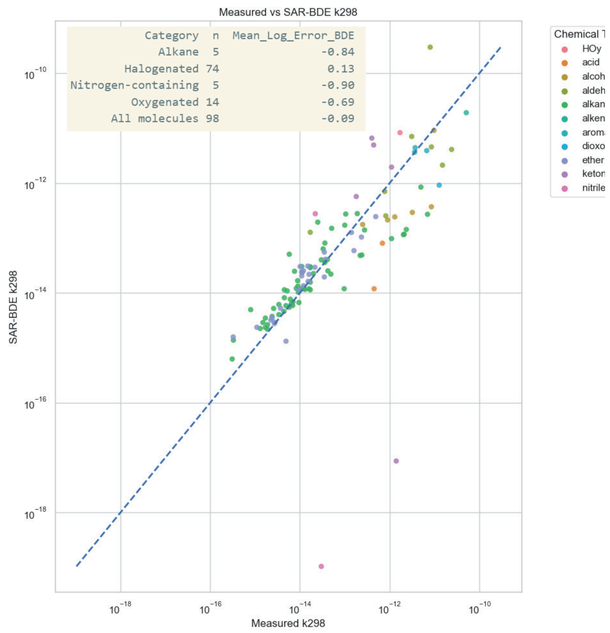

Figure 2- Measured reaction rate coefficients vs reaction rate coefficients found using computational chemistry techniques

METHODS

This study utilizes computational chemistry methods and preexisting estimates of reaction coefficients. Prior structure-activity relationships were employed to predict rate coefficients for reactions of gases with OH. To conduct this research:

- A literature search was conducted and measured OH rate coefficients at 298 K were recorded
- Predictions made using SAR-AOP (Kwok & Atkinson, 1995; Meylan & Howard, 2003) were recorded
- Gaussian was employed to calculate the bond enthalpies for each molecule, and reaction rate coefficients at 298K were calculated in excel
- Measured OH rate coefficients at 298K were compared with BDE predictions
- Two log-log scatter plots with 1:1 lines were generated using Python and color-coded based on molecule type (Figure 1 and Figure 2)
- A summary table of the statistical data was made in Python

DISCUSSION

Traditional SAR methods perform well when applied to compounds similar to those included in their training datasets, demonstrated by the strong correlation between predicted and measured k298 for simple compounds and small oxygenated species. Likewise, the computational chemistry approach demonstrates good predictive capability for compounds where hydrogen abstraction clearly dominates the reaction pathway. However, the BDE-based method exhibits greater overall deviations for certain functional groups, indicating that it does not uniformly outperform traditional SAR approaches. The reliance of SAR methods on a training dataset limits their transferability, leading to systematic inconsistencies for structurally diverse and highly fluorinated species. Conversely, the BDE-based framework is based on the established relationship between C–H bond strength and hydrogen abstraction kinetics. As a result, reduced systematic bias is observed for fluorinated hydrocarbons, suggesting improved generalizability for these compounds. Overall, both methods have many inconsistencies from actual measured rates but their accuracy depends on the chemical composition of the molecules being evaluated.

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