

Measuring OH+VOC Kinetics: A Self-Consistent, Multi-Variate Approach

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Many thousands of volatile organic compounds (VOC) have been reported as trace gases in the atmosphere.¹ The oxidation of these compounds by the ubiquitous hydroxyl radical (OH) represents a crucial, often rate-determining process in atmospheric chemistry, driving many of the atmospheric processes which have extensive impacts on human health, air pollution and climate change.² Knowledge of the bimolecular rate coefficients for these reactions is therefore fundamental to building models which can accurately simulate the complexity of the atmosphere. However, many OH + VOC reactions have not been studied in the laboratory, leading to inaccuracies within model predictions.

Rate coefficients have been traditionally determined either by absolute methods, or by comparison with well-characterised reference chemistry in the so-called “relative-rate method”. Both of these methods are extremely time consuming, requiring the study of each reaction individually. Here, we demonstrate a new method for simultaneously measuring rate coefficients for multiple VOCs. This can be combined with state-of-the-art atmospheric analytical techniques that are capable of isolating and identifying many VOC at ambient concentrations to allow for the facile estimation of novel rate coefficients for a range of different species. Comparisons with literature values for many rate coefficients for OH + VOC reactions are made using this technique to assess its validity for evaluating gas phase kinetics.

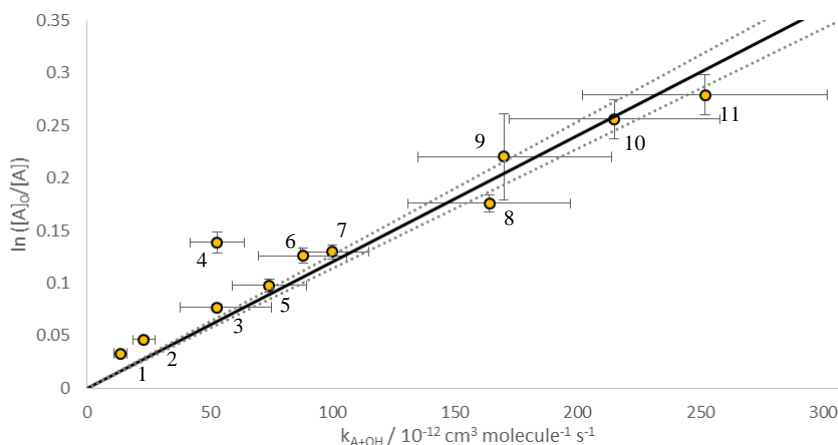


Figure 1. Relative depletion in VOC plotted against literature rate coefficients for a synthetic gas mixture with an OH reactivity of $243 \pm 20 \text{ s}^{-1}$. VOCs can be identified as follows; (1) o-xylene, (2) m-xylene, (3) α -pinene, (4) camphene*, (5) β -pinene, (6) 3-carene, (7) isoprene, (8) limonene, (9) γ -terpinene, (10) myrcene, (11) β -ocimene. The dotted-line represents one standard deviation from the weighted linear regression.

*camphene is an outlier here which may indicate that its literature rate coefficient needs to be re-evaluated.

References

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- (2) Lelieveld J.S.; Gromov, S.; Pozzer, A.; Taraborrelli D. *Atmos. Chem. Phys. Discuss.* **2016**, doi:10.5194/acp-2016-160, in review