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A new kinetics database of organic oxidation reactions for use in structure-activity relationship studies

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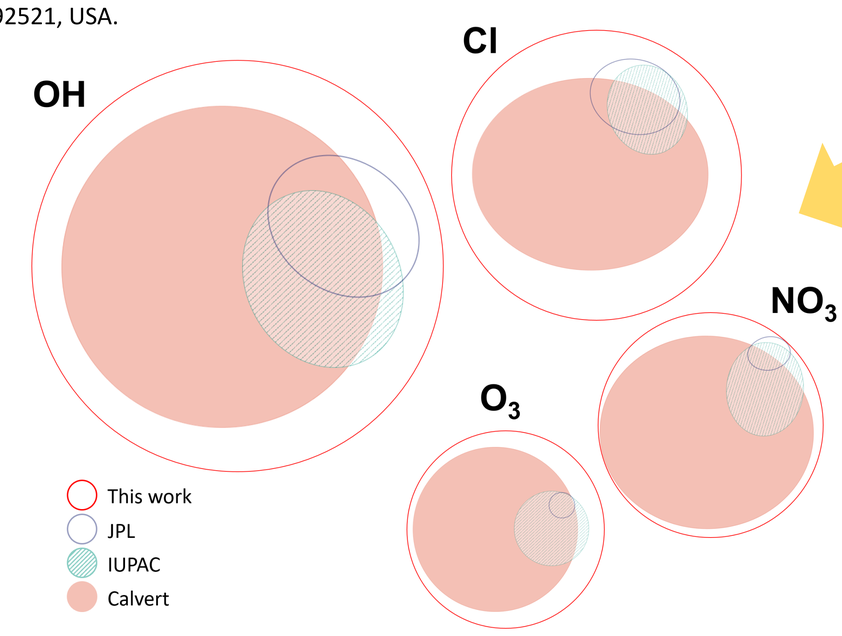
Introduction:
Several compendia of kinetic data exist, including thoroughly evaluated datasets provided by the IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation,[1-8] the JPL Panel for Data Evaluation,[9] and the Calvert et al. reviews.[10-14] The NIST Chemical Kinetics database[15] is another extensive (unevaluated) database. Despite the many useful aspects of these resources, each possess several drawbacks:

1. The frequency with which kinetic data are published is much faster than that with which these data are compiled and reviewed.
2. The number of reaction rates that have been evaluated is much smaller than the number that have been determined. It is therefore inevitable that such evaluations do not currently capture the full chemical diversity available in the experimental literature.
3. The data within these reviews are currently not downloadable in a digital, searchable format.
4. Non-downloadable databases that cannot be accessed offline are subject to downtime (e.g. NIST was recently out of commission for 38 days as a consequence of the 2018–19 US federal government shutdown)

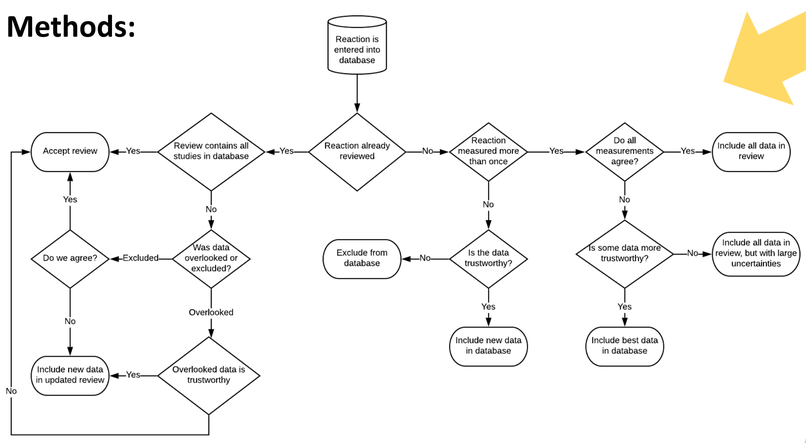


Relative coverage of databases:
Euler diagrams,[16] where the size of each curve is proportional to the number of species studied with respect to each oxidant, the number of compounds available in each review, and the overlap between these reviews

Database statistics:
Number of measurements, temperature dependence and functionality are three criteria that vary a lot between oxidants.
*hydrocarbons with no higher-order bonds are considered as 0, for halocarbons with several X substitutions, these are grouped as a single substitution.

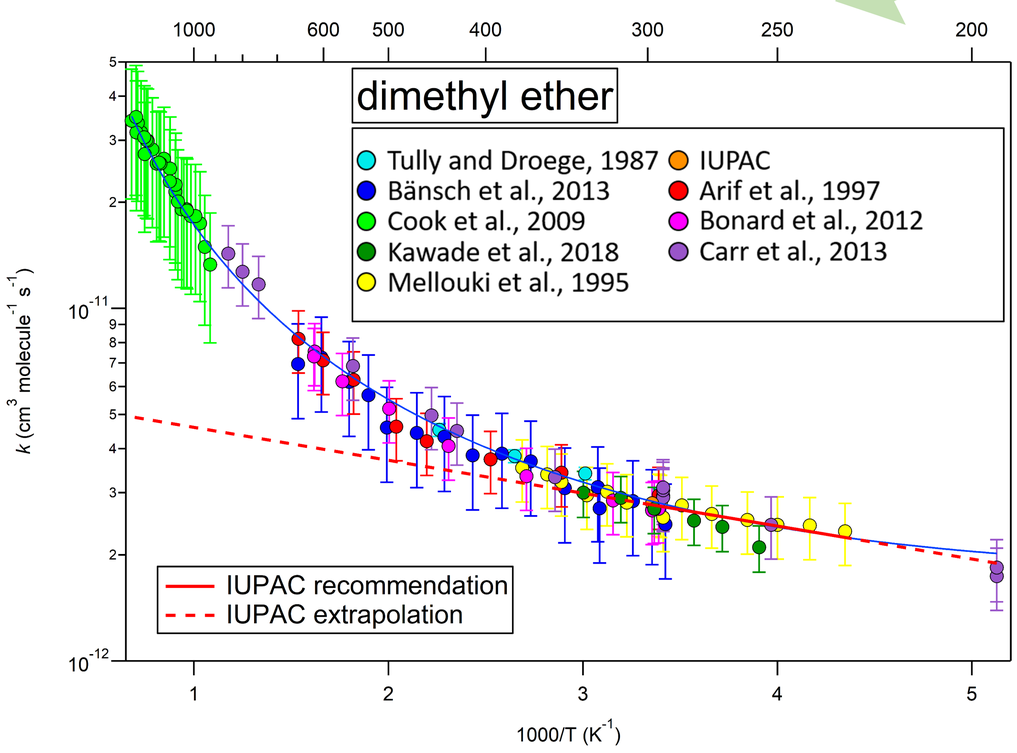
				# functional groups*						
Oxidant	# species	# Arrhenius	# Kooij	0	1	2	3	4	5	6
OH	1354	464	70	73	467	572	190	38	13	1
O_3	310	60	0	0	91	171	39	7	2	0
NO_3	389	47	0	18	154	161	46	9	1	0
Cl	708	156	3	33	271	333	56	9	5	1

Methods:

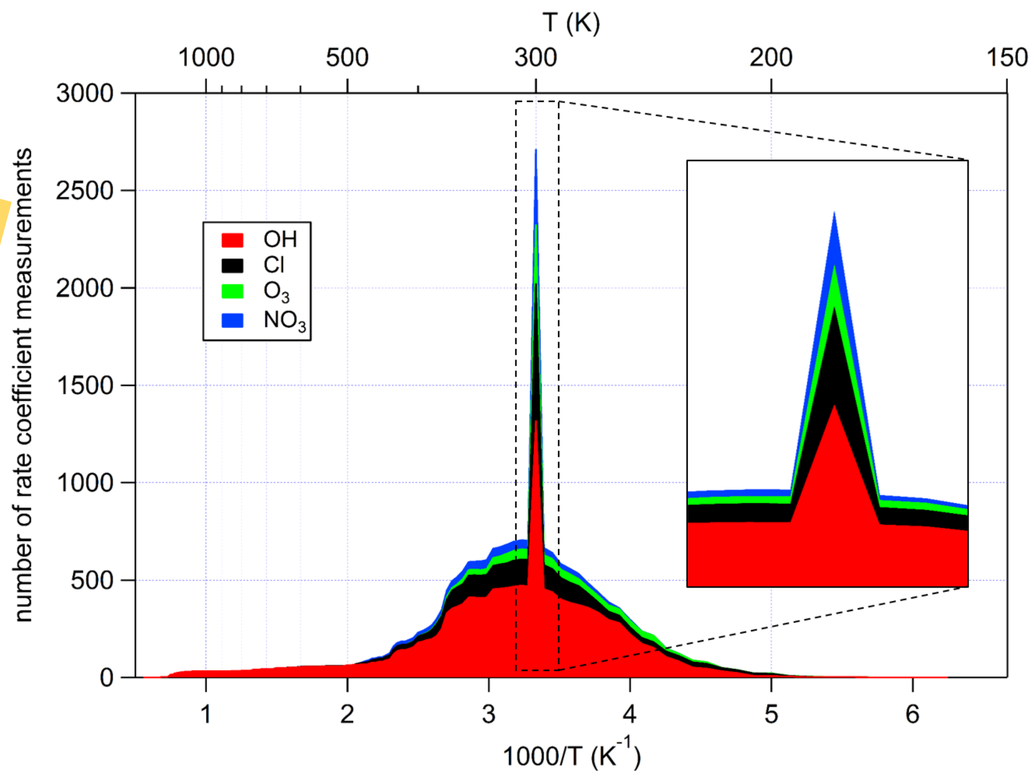


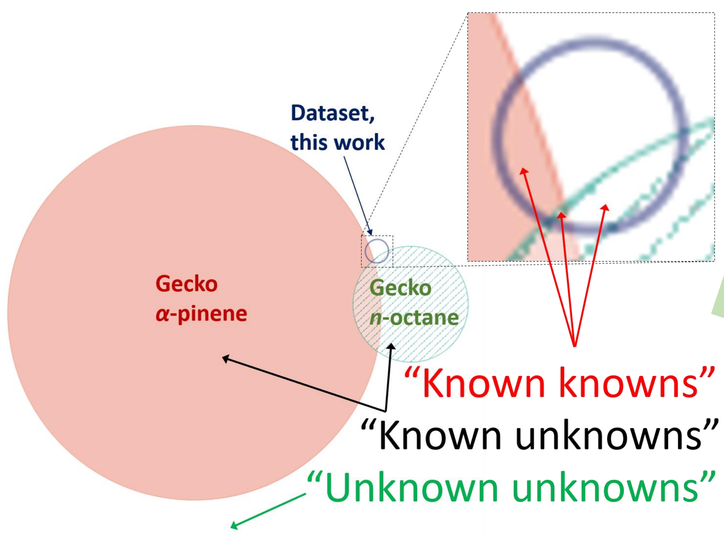
Decision tree:
The process by which our panel reviews kinetic data.

Temperature parameterization:
Where extensive temperature dependent data are reported, new parameterizations are provided, which usually take the form of Kooij's equation, such is the case for dimethyl ether.



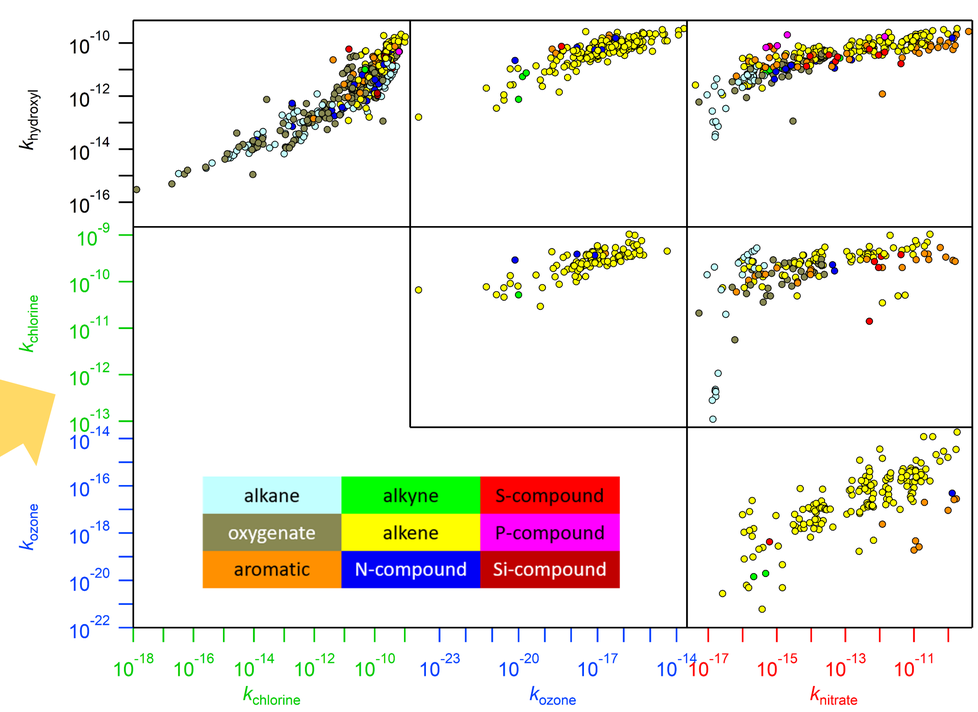
Temperature dependence:
Although a large amount of temperature-dependent data is available, the majority of species are only represented by room temperature rate coefficients. This is especially true of the NO_3 dataset, where temperature dependence has been reported for only 12% of compounds.





Overlap with atmospheric species:
An Euler diagram[16] showing the number of compounds formed from oxidation of α-pinene and *n*-octane according to the automatic mechanism generator of GECKO-A.[17] The blue circle represents the total number of compounds for which a rate coefficient has been measured. It is obvious that there are relatively few compounds that have measurements, and that the overlap is small.

Free energy relationships:
Free energy relationships of reaction rates between oxidants. Strong relationships are observed in some functionalities and oxidants (e.g. alkanes/ ethers halocarbons in the OH–Cl comparison. Sometimes very different relationships are observed depending on the functionality (e.g. alkanes vs other compounds in the NO_3–Cl comparison).



Conclusions:
1. This new database provides an updated and near-exhaustive collection of rate coefficients for the reactions of OH, Cl, NO_3 and O_3 with organic compounds.
2. This new resource will soon be available online and will be updated as new data become available.
3. Further improvements and extensions to this database are envisaged, including data for site-of-attack and reactions of other oxidants, and further experimental metadata where available.

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