CRC Report No. A-108

Development and Evaluation of Databases and Estimation Methods for Predicting Air Quality Impacts of Emitted Organic Compounds

Final Report

February 2026

COORDINATING RESEARCH COUNCIL, INC.
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Development and Evaluation of Databases and Estimation Methods for Predicting Air Quality Impacts of Emitted Organic Compounds

Final report for Contract A-108

Submitted to the Coordination Research Council
Atmospheric Impacts Committee

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SUMMARY

This report describes the activities of an international group of experts brought together in 2017 to evaluate research needs for developing comprehensive gas-phase atmospheric chemical mechanisms that reflect our current knowledge of basic chemistry and theory. The group consisted of a unique combination of expertise in experimental and theoretical atmospheric chemistry, data evaluation, atmospheric chemical mechanism development, and mechanism generation. The initial objective was evaluating and making recommendations on structure and reactivity (SAR) methods for estimating rate needed in detailed mechanisms, but this was subsequently expanded to include gathering data needed for SARs, collaborating on papers giving expert perspectives and opinions on research needs for mechanism development in general, and initiating collaborative projects on these subjects. This report describes the activities of this project from its inception to the end of the CRC-funded portion of this project at the end of 2025.

A major accomplishment of this project was the publication of three journal articles. First, giving our perspective on research needs for SARs and chemical mechanism development. Second, compiling, publishing, and making available online an evaluated and near-comprehensive database of published experimental rate parameters for reactions of VOCs with OH, NO_3, O_3, and Cl atoms under atmospheric conditions. Third, describing the use of electrotopological states to predict OH rate constants for reactions of OH with organics. A fourth paper extending the use of electrotopological states for predicting OH rate constants has been submitted and is under review. In addition, projects were initiated to: gather data on yields of products formed in VOC + OH reactions to evaluate SARs for those reactions, review estimates and treatments of photolysis reactions in mechanisms, and compile a database of theoretically calculated rate constants that are needed to develop SARs for reactions of radicals. Although the CRC-funded portion of this project has ended, the participants agree that this has been a worthwhile collaboration that should continue in some form. The prospect for ongoing work is discussed in the final chapter of this report.

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1. INTRODUCTION

Emitted organic compounds adversely affect air quality because their atmospheric reactions promote the formation of secondary pollutants such as ozone, secondary organic aerosol (SOA) and toxic organic products. Control strategies to reduce the impacts of these emissions have significant costs as well as benefits. Therefore, it is important that they be based on an ability to predict these secondary pollutants as reliably as possible. While there has been continuing research and progress in improving our knowledge of the atmospheric chemistry of organic compounds, this will not result in improved control strategies until this knowledge is incorporated into the air quality models used to develop these strategies. For this reason, the chemical mechanisms used in models should not only be as up-to-date as possible, but they should also incorporate sufficient detail to predict all the impacts of interest. Developing or assessing mechanisms for models requires developing sufficiently detailed reference mechanisms that incorporate this knowledge and best estimations based on available knowledge. Although such reference mechanisms may be too large for practical regulatory modeling, they serve as necessary starting points and standards against which to develop and evaluate condensed mechanisms optimized for specific applications. But these reference mechanisms are only as valid as the chemical knowledge and estimation methods upon which they are based.

A critical need for developing or improving detailed reference mechanisms for atmospheric chemistry is improving or evaluating the many structure-reactivity (SAR) and other estimation methods that these mechanisms require. To address this, the original objective of this project is to bring together an expert panel to evaluate the structure-reactivity or estimation methods needed to develop complete detailed mechanisms, and to make recommendations for approaches judged to be the most consistent with available knowledge. This concept was presented during the Atmospheric Chemical Mechanisms conference in Davis, California in late 2016, and a panel of international experts agreed to participate using their own funding to cover their time. Subsequently, funding was obtained from the CRC to cover administrative and travel costs for this effort. Once the project was initiated, the objective was expanded to include gathering data needed for SARs, collaborating on papers giving expert perspectives and opinions on research needs for SAR and mechanism development in general, and initiating collaborative projects on these subjects.

This report describes the activities and accomplishments of this CRC-SAR project from its inception in 2017 through the end of the CRC contract at the end of 2025. The project participants, and their roles in this project are listed in Section 1.1, the various activities and accomplishments are summarized in Section 1.2 and described in more detail in Section 2, and recommendations and plans for the future are discussed in Section 3. Although the CRC support has ended, there is still a need for this work, and the panel members believe this project has been a useful forum for communicating ideas and developing collaborative projects related to developing and evaluating SARs and detailed atmospheric mechanisms for VOCs.

1.1. Participants

The participants in this project are categorized as "full participants" and "observers". The former have the appropriate expertise and have agreed to participate and contribute to this project without compensation for their time, though in some cases they received travel reimbursement or other support using project funds when applicable. "Observers" are people of appropriate expertise who expressed an interest in the project and are copied on communications regarding the project so they can provide input when appropriate, but are unable to devote the time needed to be full participants. Table 1 gives the list of

Table 1. Summary of Project Participants (listed alphabetically within groups)

Name	Institution	Experience [a]	Status [b]
Full Participants			
Bernard Aumont	LISA, Univ. of Paris	Mech-G, MCM, EC	A
Ian Barnes	Univ. of Wuppertal	Lab, MCM, EC	Note 1
Joseph Bozzelli	New Jersey Institute of Tech.	Lab, Theory, Therm	Note 2
William Carter	Univ. of Calif. Riverside	SAR, Mech-AG, Model	A, Note 3
Mark Goldman	MIT (graduate student)	SAR, Mech-CG	Note 4
William Green	MIT	SAR, Mech-CG, Theory	Note 5
Sasha Madronich	NCAR	Mech-A, CR, Phot	A
Max McGillen	ICARE, CNRS-Orléans	SAR, Lab, Phot	A
Wahid Mellouki	ICARE, CNRS-Orléans	SAR, Lab, MCM, CR, IP, EC	A
John Orlando	NCAR	Mech-A, Lab, CR	A
Bénédicte Picquet-Varrault	LISA, Univ. of Paris	SAR, Lab, EC	A
Andrew Rickard	University of York	Mech-A, Lab, MCM, EC	A
Suarwee Snitsiriwat	Mahidol university in Thailand	Theory, Therm	Note 6
William Stockwell	University of Texas at El Paso	Mech-A, CR, Model	A
Luc Vereecken	Forschungszentrum Jülich	SAR, Mech-A, MCM, Theory	A
Tim Wallington	Ford, University of Michigan	Lab, MCM, CR, IP	A
Observers			
Richard Derwent	RDScientific	Model, CR	
Mike Jenkin	Atmos. Chem. Services	MCM, IP	
Ajith Kaduwela	California ARB	Model	Retired 2021
Deborah Luecken	U.S. EPA	Model	Retired 2019
Jozef Peeters	Univ. of Leuven (Emeritus)	Mech-A, Theory	
Michael Pilling	Univ. of Leeds (Emeritus)	Mech-AC, MCM, CR	
Chris Rabideau	Chevron	CRC Representative	
Hideto Takekawa	Toyota R&D Labs	CRC Representative	
Dudley Shallcross	University of Bristol	Mech-A, Lab	

[a] Experience codes are as follows. Note that these may be incomplete in some cases.

SAR	Published or ongoing work on SAR development
Mech-A	Development of atmospheric mechanisms
Mech-C	Development of combustion mechanisms
Mech-G	Work on existing mechanism generation software
Lab	Laboratory studies of kinetics and mechanisms
Theory	Theoretical studies of kinetics and mechanisms
Therm	Worked on thermochemistry related to kinetics
Phot	Works on photolysis reactions
MCM	Master Chemical Mechanism (MCM) advisory panel or update project
CR	Contributor to Calvert et al (2000, 2002, 2008, 2011, 2015) reviews of kinetic and mechanistic data
IP	Member of IUPAC kinetic data evaluation panel

Table 1 (continued)

EC	Involved with EUROCHAMP-2020 project for environmental chamber data
Model	Modeling applications related to chemical mechanisms

[b] Status footnotes are as follows:
- A Active participant throughout this project
- 1 Deceased January, 2018
- 2 Became an observer in 2022.
- 3 Principal investigator for the CRC program supporting this project
- 4 Mark Goldman is a student in William Green's group at MIT and represented Dr. Green in our discussions until he received his PhD and left MIT in September, 2019.
- 5 William Green became an observer in 2020.
- 6 Suarwee Snitsiriwat, previously a student of Joseph Bozzelli, joined in several group teleconferences in 2022.

participants and observers during the course of this project. Participants within each category are listed alphabetically.

Not all of the participants listed on Table 1 were active during the entire period of this project, as indicated in footnotes to the table. Except as noted, the contributions of participants in this project were supported by their own institutions or contracts, or were provided by the participants on a volunteer basis. William Carter, the Principal Investigator, was supported partially off project funds but also contributed additional time without compensation. Max McGillen was also given project funds to partially support his significant effort in leading and contributing to the experimental database project and in new SAR development. The average contributions for most project participants was ~100 hours/year for 2017-2019, the most active period of the project.

1.2. Summary of Working Groups, Activities, and Outputs

The project activities consisted primarily of periodic teleconferences and collaborative work on various papers and data gathering activities. Most communications were by email and teleconference, but several in-person meetings were held in conjunction with various kinetics or mechanism conferences. The level of activity was the highest between 2017 and 2021, but continued at a reduced level throughout the remainder of the period of this report.

The timeline of activities of the project is summarized on Table 2, and Table 3 lists the publications, presentations, and manuscripts in preparation that are attributable to this project. Note that because of the varied scope of this project and the varied expertise available, it was decided early on to form various working groups for components of this project, so not all participants were involved in producing all outputs. Table 4 lists journal articles, manuscripts in preparation and selected conference presentations that are relevant to, but not directly attributable to our project. This list is included to indicate the ongoing work of our members that addresses project objectives and that serves as inputs to our discussions.

Table 2. Timeline of activities of the SAR evaluation project.

Year	Activities
	Activities prior to the initiation of CRC Contract A-108
2016	Idea for structure-reactivity panel proposed and potential members identified.
	Presented concept for SAR project at the ACM meeting and invited attendees
2017	A total of ~20 participants agreed to participate in this project or be on its mailing list. By March, the panel consisted of 16 active members and 6 observers.
	First project teleconference held. Proposal to CRC and overall scope of the project was discussed.
	Working groups formed and initial projects identified in communications by teleconference and email.
	Work on the experimental VOC + oxidant rate constant data collection project begins.
	Activities after the initiation of CRC Contract A-108
2017	Luc Vereecken proposed we collaborate on a paper giving an overview of SARs. This began the effort that eventually led to the "Perspectives" article.
	Perspective article submitted to IJCK
	Total of 9 project teleconferences held in 2017
2018	Perspective article accepted for publication after minor revisions. We were also invited to prepare graphics concerning this article that was used for the journal cover.
	Many project participants attended the 25th International Symposium on Gas Kinetics and Related Phenomena in Lille, France. A project meeting was held in Lille prior to the conference. A poster describing this project was presented and several participants gave presentations regarding SAR issues. Luc Vereecken distributed a flyer regarding his concept for theoretical kinetic database he calls "TheoKinDB", which was inspired by activities of this project.
	Atmospheric Chemical Mechanisms meeting in Davis CA. Attended by a number of project participants, and several members gave presentations related to this project. The 2nd in-person project meeting was held.
	A total of 6 project teleconferences were held in 2018
2019	Work continued on evaluating and organizing the data in the experimental database and writing it up for publication. A manuscript describing the database was submitted to ESSD near the end of the year.
	Database made available online at EUROCHAMP web site. The database is incorporated in a spreadsheet file with search capabilities. The possibility of adding search capability and other enhancements to the web site was discussed.
	Photolysis group worked and had several teleconferences on comparing treatment of photolyses in models.
	A total of four project teleconferences were held in 2019.

Table 2 (continued)

Year	Activities
2020	The experimental database paper was published in ESSD
	Luc Vereecken reported significant progress in developing a theoretical radical rate constant database, which also includes experimental data.
	Discussions held among some members regarding scope of a general VOC SAR review.
	Atmospheric Chemical Mechanisms Conference held virtually on November 5-20. Members of our Mechanisms group co-organized a special session on mechanism development and paths forward, and gave other presentations related to this project.
	Five project teleconferences held in 2020
2021	Online VOC + oxidant rate constant database updated
	Online search capability added to the rate constant database at the Eurochamp web site.
	Five project teleconferences held in 2021
2022	Several teleconferences held regarding evaluating photolysis absorption cross sections
	Four project teleconferences held in 2022
2023	Work began on opinion paper on challenges and needs for tropospheric chemical mechanism development, led by Barbra Ervens but with most of our panel members participating.
	One project teleconference was held in 2023
2024	Paper titled "Opinion: Challenges and needs of tropospheric chemical mechanism development" published in ACP
	Two project teleconferences were held in 2024
2025	One project teleconference was held in September 2025. Several members of the CRC Atmospheric Impacts Committee attended. The consensus among members was that this has been a successful collaboration even though our activities have slowed down in recent years. Although the contract with CRC will end at the end of the year, members agreed that we should continue to meet periodically to discuss ongoing work and collaborations.

Table 3. Summary of journal articles, manuscripts, and conference presentations attributable to this project.

Title, Journal or conference, Authors	Relevance to Project
Published journal articles	
Perspective on Mechanism Development and Structure-Activity Relationships for Gas-phase Atmospheric Chemistry Int. J. Chem. Kinet., 50, 435-469, 2018. DOI: 10.1002/kin.21172. L. Vereecken, B. Aumont, I. Barnes, J. W. Bozzelli, M. J. Goldman, W. H. Green, S. Madronich, M. R. McGillen, A. Mellouki, J. J. Orlando, B. Picquet-Varrault, A. R. Rickard, W. R. Stockwell, T. J. Wallington, and W. P. L. Carter	See Section 2.1
Database for the kinetics of the gas-phase atmospheric reactions of organic compounds Earth Syst. Sci. Data, 12, 1203-1216, 2020. https://doi.org/10.5194/essd-12-1203-2020 M. R. McGillen., W. P. L. Carter, A. Mellouki, J. J. Orlando, B. Picquet-Varrault, and T. J. Wallington	See Section 2.2.
Opinion: Challenges and needs of tropospheric chemical mechanism development Atmos. Chem. Phys., 24, 13317–13339, 2024. Https://doi.org/10.5194/acp-24-13317-2024 B. Ervens, A. Rickard, B. Aumont, W. P. L. Carter, M. McGillen, A. Mellouki, J. Orlando, B. Picquet-Varrault, Paul Seakins, W. R. Stockwell, L. Vereecken, and T. J. Wallington	See Section 2.3.
The use of the electrotopological state as a basis for predicting hydrogen abstraction rate coefficients: a proof of principle for the reactions of alkanes and haloalkanes with OH Environ. Sci. Atmos, 4, 18-34, 2024. DOI: 10.1039/d3ea00147d M. R. McGillen., L,. Michalat, J. J. Orlando, and W. P. L. Carter	See Section 2.4
Manuscripts submitted or in preparation	
Estimating Rate Coefficients for the Reactions of Ethers + OH from Atmospheric to Combustion Temperatures: An extension of the Electrotopological State Method Submitted to Environ. Sci. Atmos. December 10, 2025 L. Michelat, J. J. Orlando, W. P.L. Carter, and M. R. McGillen	See Section 2.5
The use of OH/VOC ‘site-specific’ rate coefficients and branching ratios to test and improve Structure – Reactivity Relationships In preparation. Complete draft exists and is being reviewed by authors. J. J. Orlando, W. P. L. Carter, M. R. McGillen, B. Aumont	See Section 2.6.

Table 3 (continued)

Title, Journal or conference, Authors	Relevance to Project
Selected onference presentations	
A new database for the kinetics of the gas-phase atmospheric reactions of organic compounds Presented at the Atmospheric Chemical Mechanism (ACM) Conference, virtual, November 5-20, 2020. M. R. McGillen	See Section 2.2.
Structure-Activity Relations for Organic Photo-processes, Part 1: Absorption Cross Sections Presented at the Atmospheric Chemical Mechanism Conference, virtual, November 5-20, 2020. Sasha Madronich	See Section 2.8.

Table 4. Journal articles, conference presentations or manuscripts in preparation involving group members that are relevant to, but not direct outputs of this project

Title, Journal or conference, Authors	Relevance to Project
Unimolecular decay strongly limits Criegee intermediate concentration in the atmosphere Phys. Chem. Chem. Phys., 19, 31599-31612, 2017. DOI:10.1039/C7CP05541B L. Vereecken, A. Novelli, D. Taraborrelli	Reports on new extensive SARs for reactions of Criegee intermediates.
Review of the SAPRC-16 Chemical Mechanism and Comparison with the Regional Atmospheric Chemistry Mechanism, Version-2 Presented at the Atmospheric Chemical Mechanism Conference, Davis, California, December 5-7, 2018 W. R. Stockwell	Discusses the updated SAPRC, RACM2 and GACM mechanisms and how they differ, the SAPRC mechanism generation system, and general issues regarding mechanisms.
Estimation of rate coefficients and branching ratios for gas-phase reactions of OH with aliphatic organic compounds for use in automated mechanism construction Atmos. Chem. Phys., 18, 9297–9328, 2018. https://doi.org/10.5194/acp-18-9297-2018 M. E. Jenkin, R. Valorso, B. Aumont, A. R. Rickard, and T. J. Wallington	First of three papers that describe SARs for initial VOC reactions that are implemented in updated GECKO-A as part of the MAGNIFY (2018) project to update MCM.

Table 4 (continued)

Title, Journal or conference, Authors	Relevance to Project
Estimation of rate coefficients and branching ratios for gas-phase reactions of OH with aromatic organic compounds for use in automated mechanism construction Atmos. Chem. Phys., 18, 9329–9349, 2018. https://doi.org/10.5194/acp-18-9329-2018 M. E. Jenkin, R. Valorso, B. Aumont, A. R. Rickard, and T. J. Wallington	Second of three papers on VOC SARs for MCM/GECKO-A. See above
Estimation of rate coefficients and branching ratios for reactions of organic peroxy radicals for use in automated mechanism construction Atmos. Chem. Phys., 19, 7691-7717, 2019. https://doi.org/10.5194/acp-19-7691-2019 M. E. Jenkin, R. Valorso, B. Aumont, and A. R. Rickard	Gives updated SARs for peroxy radical reactions for implementation in updated GECKO-A as part of the MAGNIFY (2018) project to update MCM.
Reaction Mechanisms for the Atmospheric Oxidation of Monocyclic Aromatic Compounds Advances in Atmospheric Chemistry, Volume 2: Organic Oxidation and Multiphase Chemistry, World Scientific Publishing Co., 2019. https://doi.org/10.1142/11031 L. Vereecken	Discusses theoretical calculations and SARs relevant to the atmospheric reactions of aromatics and the intermediates formed.
Estimation of rate coefficients for the reactions of O_3 with unsaturated organic compounds for use in automated mechanism construction Atmos. Chem. Phys., 20, 12921–12937, 2020. https://doi.org/10.5194/acp-20-12921-2020 M. E. Jenkin, R. Valorso, B. Aumont, M. J. Newland, and A. R. Rickard	Third of three papers on VOC SARs for MCM/GECKO-A. See above
A Perspective on the Development of Gas-phase Chemical Mechanisms for Eulerian Air Quality Models J. Air Waste Manage. Assoc., 70, 44–70, 2020. doi:10.1080/10962247.2019.1694605 W. R. Stockwell, E. Saunders, W.S. Goliff and R.M. Fitzgerald	Provides a history of mechanism development practices and an overview of selected schemes for research and air quality modeling.
Presentations on MCM, SAPRC, and RACM2/GACM mechanisms Presented at the Atmospheric Chemical Mechanism Conference, virtual, November 5-20, 2020. Separate presentations by A. Rickard, W. Carter, W. Stockwell and W. Goliff.	Gave presentations on latest versions of these mechanisms and discussed general issues on mechanism development and use of SARs and mechanism generation.
H-migration in peroxy radicals under atmospheric conditions Atmospheric Chem. Phys., 2020, 20, 7429–7458, 2020. https://doi.org/10.5194/acp-20-7429-2020 L. Vereecken and B. Nozière	Presents experimental and theoretical data on H-shift isomerizations of peroxy radicals and describes a new SAR for these reactions

Table 4 (continued)

Title, Journal or conference, Authors	Relevance to Project
Estimation of Rate Constants for Reactions of Organic Compounds under Atmospheric Conditions Atmosphere 2021, 12, 125. https://doi.org/10.3390/atmos12101250 W. P. L. Carter	Paper on SARs to estimate VOC rate constants used in the SAPRC mechanism and mechanism generation system (MechGen).
Theoretical and experimental study of peroxy and alkoxy radicals in the NO_3-initiated oxidation of isoprene Phys. Chem. Chem. Phys., 23, 5496-5515 2021. https://doi.org/10.1039/D0CP06267G L. Vereecken, P. Carlsson, A. Novelli, F. Bernard, S. S. Brown, C. Cho, J. Crowley, H. Fuchs, W. Mellouki, D. Reimer, J. Shenolikar, R. Tillmann, L. Zhou, A. Kiendler-Scharr, and A. Wahner	Discuss theoretical calculations of reactions of alkoxy and peroxy radicals formed in the isoprene oxidation system, and compares them with published SARs. Also discusses related experimental data.
Experimental and theoretical study on the impact of a nitrate group on the chemistry of alkoxy radicals Phys. Chem. Chem. Phys., 23, 5474-5495, 2021. https://doi.org/10.1039/D0CP05555G A. Novelli, C. Cho, H. Fuchs, A. Hofzumahaus, F. Rohrer, R. Tillmann, A. Kiendler-Scharr, A. Wahner, L. Vereecken	Describes calculations and experimental data on reactions of nitrated alkoxy radicals. Extends alkoxy SARs and provide guidance for alkoxy H-migration reactions.
A structure activity relationship for ring closure reactions in unsaturated alkylperoxy radicals Phys. Chem. Chem. Phys., 23, 16564-16576, 2021. https://doi.org/10.1039/D1CP02758A L. Vereecken, G. Vu, A. Wahner, A. Kiendler-Scharr, H. M. T. Nguyen	Derives a SAR for a type of unimolecular peroxy radical reaction that has not previously been systematically considered.
Unimolecular and water reactions of oxygenated and unsaturated Criegee intermediates under atmospheric conditions Phys. Chem. Chem. Phys., 24, 6428-6443, 2022. https://doi.org/ 10.1039/D1CP05877K L. Vereecken, A. Novelli, A. Kiendler-Scharr., A. Wahner	Reports on new extensive SARs for reactions of oxygenated and unsaturated Criegee intermediates.
Derivation of atmospheric reaction mechanisms for volatile organic compounds by the SAPRC mechanism generation system (MechGen) Atmospheric Chemistry and Physics, 25(1), 199-242. https://doi.org/10.5194/acp-25-199-2025 W. P. L. Carter., J. Jiang, J. J. Orlando, K. Barsanti	Paper on other SARs, estimates, and assignments used to derive detailed mechanisms using the SAPRC mechanism generation system.
The SAPRC Atmospheric Chemical Mechanism Generation System (MechGen) Geosci. Model Dev., 18, 8461–8483, 2025. https://doi.org/10.5194/gmd-18-8461-2025 W. P. L. Carter. J. Jiang, Z. Wang, and K.C. Barsanti	Paper on the SAPRC mechanism generation system software. This software is available online and was used to derive recent SAPRC mechanisms.

Table 4 (continued)

Title, Journal or conference, Authors	Relevance to Project
GECKO-A / MechGen Comparison Paper (preliminary working title) In Preparation J. Lee-Taylor, J. J. Orlando, W. P. L. Carter, B. Aumont, K. C. Barsanti1, Z. Wang, Marie Camredon, and R. Valorso	Shows differences in SARs and estimation methods used for two mechanism generation systems. Draft mostly complete.

2. DISCUSSION OF INDIVIDUAL PROJECTS

In this section, we will provide more information about individual projects carried out as part of work for this program. These projects have various levels of completion, with some resulting in published journal articles, some resulting in papers that are under review or nearing completion, some with results that have not yet been published, and some where work is still underway or being considered for the future. Although the CRC program covered by this report has ended, it is expected that some of these collaborative projects will continue, as discussed in Section 3.

2.1. 2018 Perspectives Article

Several months after the initiation of this project, Luc Vereecken suggested that the group work on a "Perspectives" article to be submitted to the International Journal of Chemical Kinetics (IJCK). The idea of this paper is to provide a general overview of what could be improved in atmospheric kinetic modeling, with emphasis specifically topics this SAR panel is working on. This idea was accepted by the group as a good start for the project, and all active participants at the time contributed as co-authors.

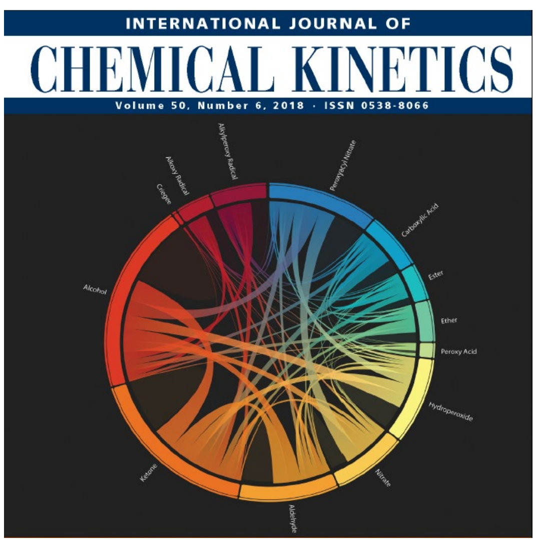
The paper was accepted for publication in March, 2018 and published in April. The title, journal information, authors, and abstract are summarized on Table 5. The Journal felt that the article was significant enough to merit a cover image on the journal, and one was prepared and accepted. The image is included in Table 5.

2.2. VOC + Oxidant Rate Constant Database

The second major accomplishment of this project was compiling and publishing a computer-readable database of evaluated experimentally measured rate constants for the gas-phase reactions of organic compounds with OH and NO_3 radicals, O_3 and Cl atoms. The objective was to compile as complete a set of recommended rate constants as possible given the available data, so it can be used for the development of SARs and other applications requiring rate constants for multiple compounds, as well as serving as a general resource for the research community. Ideally, the best approach would be for us to carry out independent evaluations of the data for each compound and reaction and make our own recommendations. However, the group decided that this is not practical for the near term given the resources available to this project, and our desire to have a database soon that we can make available to the kinetics community and use it for SAR evaluations to address the primary objectives of the project. Therefore, we focused our efforts at this phase of the project on choosing which of the evaluations to use for the recommended rate parameters, and make our own evaluations and add primary measurements to the database if new data are available that make existing evaluations out of date. The contents of the latest version of the database is summarized on Table 6.

A journal article describing our initial work on the database was published in the Earth System Science Data (ESSD) journal in 2020, and is summarized on Table 6. This database was made available on the Eurochamp Web site as also indicated on the table. This publication of this article and the associated online data was not the end of this project. Data collection and evaluation considered throughout the remainder of this project, and the online database was updated several times. In addition, a search capability was added to the online system in 2021. The cost for the programming for this search capability was originally to be covered by project funds, but Eurochamp did not charge us for this effort.

Table 5. Information and abstract of the IJCK Perspectives article published in 2018

<table>
<tr><td>Title</td><td colspan="2">Perspective on Mechanism Development and Structure-Activity Relationships for Gas-phase Atmospheric Chemistry</td></tr>
<tr><td>Authors</td><td colspan="2">L. Vereecken, B. Aumont, I. Barnes, J. W. Bozzelli, M. J. Goldman, W. H. Green, S. Madronich, M. R. McGillen, A. Mellouki, J. J. Orlando, B. Picquet-Varrault, A. R. Rickard, W. R. Stockwell, T. J. Wallington, and W. P. L. Carter</td></tr>
<tr><td>Journal</td><td colspan="2">Int. J. Chem. Kinet., 50, 435-469, 2018. DOI: 10.1002/kin.21172.</td></tr>
<tr><td>Abstract</td><td colspan="2">This perspective gives our views on general aspects and future directions of gas-phase atmospheric chemical kinetic mechanism development, emphasizing on the work needed for the sustainable development of chemically detailed mechanisms that reflect current kinetic, mechanistic, and theoretical knowledge. Current and future mechanism development efforts and research needs are discussed, including software-aided auto-generation and maintenance of kinetic models as a future-proof approach for atmospheric model development. There is an overarching need for the evaluation and extension of Structure-Activity Relationships (SARs) that predict the properties and reactions of the many multi-functionalized compounds in the atmosphere that are at the core of detailed mechanisms, but for which no direct chemical data are available. Here, we discuss the experimental and theoretical data needed to support the development of mechanisms and SARs, the types of SARs relevant to atmospheric chemistry, the current status and limitations of SARs for various types of atmospheric reactions, the status of thermochemical estimates needed for mechanism development, and our outlook for the future. The authors have recently formed a SAR evaluation working group to address these issues.</td></tr>
<tr><td>Journal Cover Image</td><td>
</td><td>The image gives a visualization of the complex range of multifunctional species in MCMv3.3.1, which contains ~7,600 species and ~17,000 reactions. Links for multifunctional species containing at least one of the functional groups indicated are shown.

The image was prepared by Daniel Ellis and Andrew Rickard of the University of York.</td></tr>
</table>

Table 6 gives a summary of the database at the time of the latest update in 2023, which is the version that is currently available online. The data are still being compiled as new rate constant measurements are published, primarily due to the efforts of Max McGillen. The plan is to continue with this data collection and database update, with the next update publication planned for 2026.

Table 6. Summary of the latest version of the VOC experimental rate constant database.

Compound or Item Types	Numbers of Compounds or Items				
	Total	k(OH)	k(O_3)	k(NO_3)	k(Cl)
Hydrocarbons	304	242	135	138	105
Oxygenates	560	494	129	191	266
Oxidized nitrogen [a]	98	92	8	2	47
Halogenated hydrocarbons	227	204	31	30	120
Halogenated oxygenates	196	154	-	2	144
Amines	82	81	6	12	12
Other types of compounds	102	89	5	20	40
Total number of rate constant entries	5238	2752	563	685	1238
T=298K rate constant recommendations	2799	1356	314	395	734
T dependence recommendations	821	560	60	45	156
Recommendations for T>298K only	10	7	2	-	1

[a] Includes organic nitrates, nitro compounds, peroxynitrates, and nitrites.

2.3. 2024 ACP Opinion Article

In 2023 our member Andrew Rickard invited our group to participate in an opinion article on atmospheric chemical mechanism development that he and some of his colleagues were considering for submission as a highlight paper in an anniversary article for the journal Atmospheric Chemistry. Most of our active members at the time participated in the preparation of this article, under the leadership of Barbara Ervens of CNRS in France. This paper was published in 2024 and is summarized on Table 7.

2.4. First Article on Using Electrotopological States for Predicting OH Rate Constants

In part as a result of discussions among our group, our member Max McGillen led an effort to investigate new methods for deriving SARs for site-specific VOC + OH rate constants that are an alternative to the empirical "Atkinson" group additivity method (e.g., Kwok and Atkinson, 1995) that currently available online (EPA-2020) and used in current mechanism generation systems (e.g., Jenkin et al, 2018a and Carter, 2021 -- see Section 2.7). It has been known for some time that these methods perform poorly in predicting H-abstraction rate constants for highly halogenated compounds, which is attributable to long-range interactions that cannot be adequately represented without using an excessive number of adjustable parameters. McGillen and colleagues discovered that the electrotopological state (E-state), a fundamental property that can describe the substituent effect upon each hydrogen environment in a molecule (Hall and Kier, 1995), can be a basis of a new method for estimating H-abstraction rate constants from alkanes and haloalkanes that performs significantly better and with fewer adjustable

Table 7. Information and abstract of the ACP opinion article published in 2024

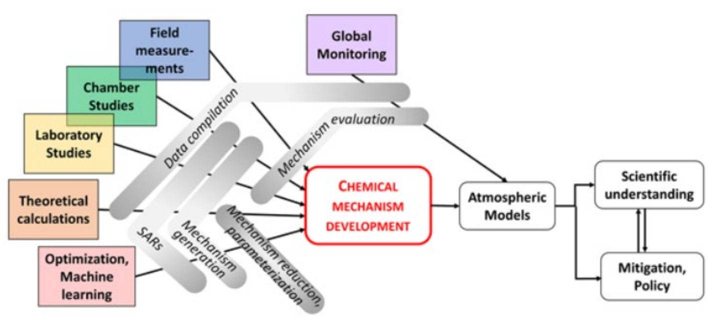
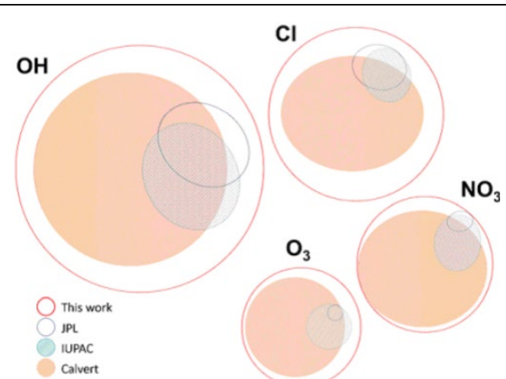
Title	Opinion: Challenges and needs of tropospheric chemical mechanism development
Authors	B. Ervens, A. Rickard, B. Aumont, W. P. L. Carter, M. McGillen, A. Mellouki, J. Orlando, B. Picquet-Varrault, Paul Seakins, W. R. Stockwell, L. Vereecken, and T. J. Wallington
Journal	Atmos. Chem. Phys., 24, 13317–13339, 2024. Https://doi.org/10.5194/acp-24-13317-2024
Abstract	Chemical mechanisms form the core of atmospheric models to describe degradation pathways of pollutants and ultimately inform air quality and climate policymakers and other stakeholders. The accuracy of chemical mechanisms relies on the quality of their input data, which originate from experimental (laboratory, field, chamber) and theoretical (quantum chemistry, theoretical kinetics, machine learning) studies. The development of robust mechanisms requires rigorous and transparent procedures for data collection, mechanism construction and evaluation and the creation of reduced or operationally defined mechanisms. Developments in analytical techniques have led to a large number of identified chemical species in the atmospheric multiphase system that have proved invaluable for our understanding of atmospheric chemistry. At the same time, advances in software and machine learning tools have enabled automated mechanism generation. We discuss strategies for mechanism development, applying empirical or mechanistic approaches. We show the general workflows, how either approach can lead to robust mechanisms and that the two approaches complement each other, resulting in reliable predictions. Current challenges are discussed related to global change, including shifts in emission scenarios that result in new chemical regimes (e.g., low-NO scenarios, wildfires, mega- and gigacities) and that require the development of new or expanded gas- and aqueous-phase mechanisms. In addition, new mechanisms should be developed to also target oxidation capacity and aerosol chemistry impacting climate, human and ecosystem health.
Image shown with article	 Research activities connected to chemical mechanism development for implementation in atmospheric models, leading to an enhanced understanding of atmospheric implications eventually resulting in adequate air quality and climate policies.

Table 8. Information and abstract of the ESST VOC kinetics database article published in 2020

Title	Database for the kinetics of the gas-phase atmospheric reactions of organic compounds
Authors	M. R. McGillen., W. P. L. Carter, A. Mellouki, J. J. Orlando, B. Picquet-Varrault, and T. J. Wallington
Journal	Earth Syst. Sci. Data, 12, 1203-1216, 2020. https://doi.org/10.5194/essd-12-1203-2020
Abstract	We present a digital, freely available, searchable, and evaluated compilation of rate coefficients for the gas-phase reactions of organic compounds with OH, Cl, and NO3 radicals and with O3. Although other compilations of many of these data exist, many are out of date, most have limited scope, and all are difficult to search and to load completely into a digitized form. This compilation uses results of previous reviews, though many recommendations are updated to incorporate new or omitted data or address errors, and includes recommendations on many reactions that have not been reviewed previously. The database, which incorporates over 50 years of measurements, consists of a total of 2765 recommended bimolecular rate coefficients for the reactions of 1357 organic substances with OH, 709 with Cl, 310 with O3, and 389 with NO3, and is much larger than previous compilations. Many compound types are present in this database, including naturally occurring chemicals formed in or emitted to the atmosphere and anthropogenic compounds such as halocarbons and their degradation products. Recommendations are made for rate coefficients at 298 K and, where possible, the temperature dependences over the entire range of the available data. The primary motivation behind this project has been to provide a large and thoroughly evaluated training dataset for the development of structure–activity relationships (SARs), whose reliability depends fundamentally upon the availability of high-quality experimental data. However, there are other potential applications of this work, such as research related to atmospheric lifetimes and fates of organic compounds, or modelling gas-phase reactions of organics in various environments. This database is freely accessible at https://doi.org/10.25326/36 (McGillen et al., 2019).
Image shown with article	 Area-proportional Venn diagrams with the size and position 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
URLs for data	Searchable (2021 data) https://data.eurochamp.org/data-access/kin/#/data Latest (2023) data https://data.eurochamp.org/sar-database/

parameters. This work is reported in a journal article that was published in 2024 and summarized on Table 9. This is the first of two journal articles on this subject, with the second one, which is now under review, being described in the following section.

2.5. Second Paper on Using Electrotopological States for Predicting OH Rate Constants

The first paper on the E-state method for estimating OH abstraction rate constants covered only alkanes and haloalkanes, but in principle this method could be extended to saturated compounds with oxygen or other atoms by using the electrotopological state for those other atoms (Hall and Kier, 1995). However, this approach was found to systematically underestimate rate constants for many ethers. This is attributed to the formation of van der Waals (vdW) pre-reactive complexes that facilitate H-abstraction reactions. McGillen and co-workers developed a method to take possible formation of these complexes into account and give much better estimates of rate constant for ethers and haloethers. Some of the work for developing the necessary software was supported in part using funds from this project. The paper describing the extension of this method to ethers and haloethers was submitted in late 2025 to the same journal that published the first paper, and is summarized on Table 9. Work on extending this method to other classes of compounds is expected to continue.

2.6. Paper in Preparation on a "Site of Attack" Database for OH + VOC reactions

The VOC + Oxidant database developed in this program can provide a means to develop and evaluate based on predictions of total rate constants, but do not provide direct information on site-specific rate constants, or branching ratios, when more than one reaction can occur when the oxidant reacts with the compound. Site-specific rate constants can be inferred based on predictions of total rate constants for a variety of compounds, if it is assumed that rate constants for reactions at a particular site with similar substituents are the same within different molecules, which is the basis of most VOC + oxidant SARs. However, this is an indirect method for deriving ratios of site-specific rate constants, and the assumptions required by this method may not necessarily always be correct.

A potentially more direct method to evaluate SAR predictions of branching ratios is to measure yields of product formed from the completing reactions and use experimentally measured product yield ratios as an indicator of the branching ratio. This requires the assumption that reaction at each site forms a unique product (or set of products) in approximately 100% yield, that consumption of the product by secondary reactions during the product yield experiment is either minor or can be corrected for, and that that product is not formed from reactions at other sites or from secondary reactions of other products. Although this is not always the case, it is often the case for many types of experiments and reactions.

There is a body of published studies of measurements of products and product yields from reactions of organic compounds with OH radicals under atmospheric conditions, but these data have not been compiled for use of systematic studies of SARs for VOC + OH reactions. Led by our group members Bernard Aumont and John Orlando, in collaboration with other members of our group, have compiled a database of experimentally measured product yields from VOC + OH reactions that can be used to derive branching ratios for these reactions, and then used these data to evaluate the branching ratio predictions of the SARs used in the SAPRC and GECKO-A mechanism generation systems. Bernard Aumont gave a presentation giving preliminary results in a conference in 2018, and an example of the results presented is shown in Figure 1. This data collection and analysis continued during the course of this project, and a paper describing this work has been drafted and is expected to be submitted sometime during the first quarter of 2026. This manuscript is summarized on Table 11. Possible additional work in this area is discussed in Section 3.

Table 9. Information and abstract of the first article on using electrotopological states for estimating OH abstraction rate constants, published in 2024

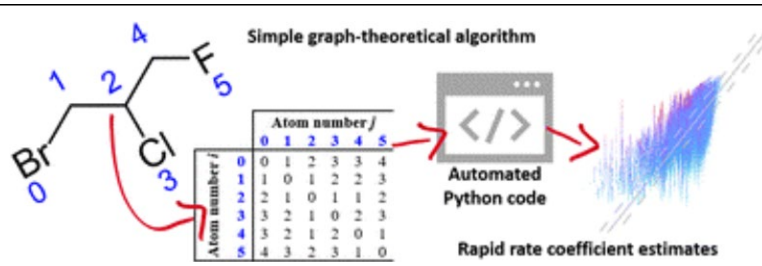
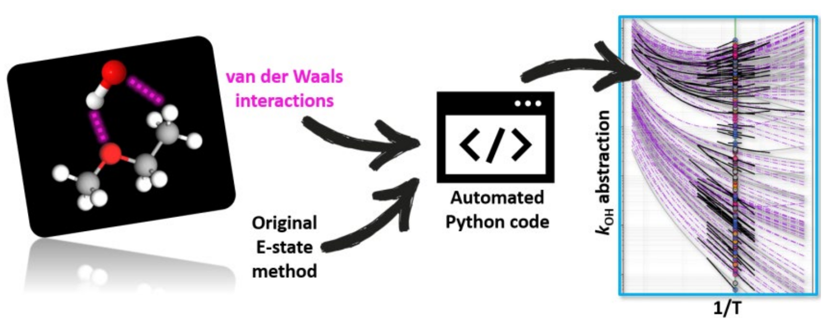
Title	The use of the electrotopological state as a basis for predicting hydrogen abstraction rate coefficients: a proof of principle for the reactions of alkanes and haloalkanes with OH
Authors	M. R. McGillen., L. Michalat, J. J. Orlando, and W. P. L. Carter
Journal	Environ. Sci. Atmos, 4, 18-34, 2024. DOI: 10.1039/d3ea00147d
Abstract	Structure–activity relationships (SARs) are essential components of detailed chemical models, where they are employed to provide kinetic information when high-quality experimental or theoretical data are unavailable. Notwithstanding, there are very few types of SARs that are routinely employed to estimate reaction kinetics. Accordingly, a new temperature-dependent and site-specific technique for rate coefficient estimation is presented, based on the electrotopological state (E-state), a fundamental property that can describe the substituent effect upon each hydrogen environment in a molecule. This accounts for the electronic character of individual atoms within molecules and their respective distances from one another. This method is applied to the hydrogen abstraction reactions of OH with alkanes and haloalkanes, where it was found to perform well compared with other approaches for molecules whose rate coefficients have been measured experimentally over a broad temperature range (~200–1500 K). To extend this comparison, an efficient software tool for batch-estimated rate coefficients has been developed. By applying this software to fully enumerated lists of halocarbons containing from one to four carbon atoms, we were able to compare predictions of >100 000 species between techniques, and although experimental coverage is sparse, we could assess the degree of consensus between these estimates. Disagreement between methods was found to increase with carbon number, and differences of up to three orders of magnitude were observed in some cases. The reasons for these discrepancies and possible solutions are discussed. In a further demonstration of the utility of the E-state approach, we show that it can also be used to calculate bond-dissociation energy (BDE), which also compares favourably with a state-of-the-art literature method. The E-state approach not only provides accurate predictions of rate coefficients, but it does so with fewer fitting parameters and by being constrained by a fundamental molecular property. From this we conject that it is less prone to overfitting and more easily expanded to unfamiliar substituents than previous SAR approaches. The efficiency and robustness with which estimates of BDE and rate coefficients are made over a wide range of conditions will be of relevance to a variety of fields including atmospheric and combustion chemistry
Image shown with article	

Table 10. Information and abstract of the second article on using electreotopological states for estimating OH abstraction rate constants, submitted in late 2025

Title	Estimating Rate Coefficients for the Reactions of Ethers + OH from Atmospheric to Combustion Temperatures: An extension of the Electrotopological State Method
Authors	L. Michelat J. J. Orlando, W. P.L. Carter, and M. R. McGillen
Journal	Submitted to Environ. Sci. Atmos. December 10, 2025
Abstract	The reactions of ethers with OH present a challenge to estimation techniques. These hydrogen abstraction reactions exhibit both positive and negative temperature dependences according to temperature regime and degree of halogenation. Positive temperature dependence relates to reactants overcoming energy barriers in the primary process of hydrogen abstraction, and is readily described using a recently developed structure-activity relationship based upon the electrotopological state (E-state). Conversely, we attribute the negative temperature dependence to the formation of van der Waals (vdW) pre-reactive complexes that facilitate reactions through quantum tunnelling, for which we have developed a simple parameterization. This is implemented in the current version of the E-state code in a modular fashion, leaving the original parameterization for alkanes and haloalkanes unmodified. We find that this treatment combined with the a priori information provided by the E-state affords, to some extent, the decoupling of these opposing behaviours leading to a robust prediction of temperature-dependent rate coefficients with OH, k(T), compared with existing methodologies. This approach, named E-stateXvdW, provides site-specific, temperature-dependent estimates implemented in a freely available open-source Python programme that can estimate large batches of compounds automatically and at negligible computational cost over a broad temperature range (~190–1500 K). This method applies to all acyclic non-halogenated and halogenated ethers of composition CnO≤n–1HmX2n+2–m, and provisionally, all cyclic ethers of composition CnO≤n–1HmX2n–m, where X represents any combination of F, Cl, Br and I, n = [1, 2, …] and m = [1, 2, …, 2n + 2]. This approach may be useful to modellers and environmental scientists who wish to assess the fate of industrially important etheric molecules, as well as those chemists with an interest in rationalizing the reactivity of molecules based on their structural characteristics.
Image submitted with article	

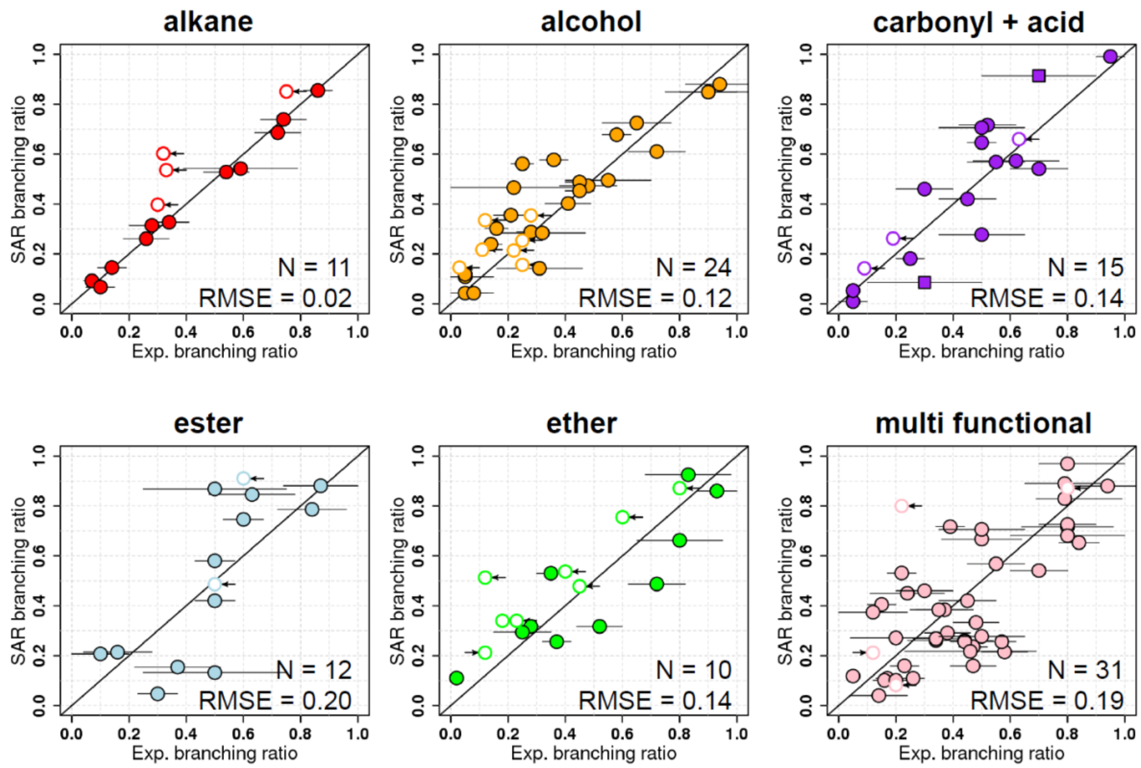


Figure 1. Comparisons from the presentation by Bernard Aumont (2018) showing the use of the "Site of Attack" relative OH rate constant database for SAR evaluation.

2.7. Comparison of SAPRC and GECKO-A Organic Reaction SARs

As part of our evaluations of existing SARs, we compared the predictions of the VOC SARs used in the SAPRC MechGen (Carter, 2021; Carter et al 2025a,b) and GECKO-A (Aumont et al, 2005) mechanism generation systems. The updated SARs developed for MCM/GECKO-A include SARs for reactions of organics with OH (Jenkin et al, 2018a,b), NO_3 (Kerdouci et al, 2014) and O_3 (Jenkin et al, 2020). Both sets of SARs cover the major types of organics represented in current atmospheric models, including hydrocarbons, oxygenates, organic nitrates, and bi- or polyfunctional compounds containing oxygenate and/or nitrate groups. The SAPRC SARs include additional classes of compounds, but this comparison is restricted to those compounds whose rate constants can be predicted by both sets of SARs.

Note that both sets of SARs were developed independently, though the approaches employed were similar. In both cases, the SARs employ base rate constants for each group in the molecule, where a group is a carbon atom with an abstractable hydrogen or with a double or triple bond where the oxidant species can add, with correction factors applied based on the presence of neighboring groups, or based on structural characteristics such as the presence of rings, and with the group rate constants and correction factors optimized to minimize errors in SAR predictions. However, the MCM/GECKO-A SARs tend to have more corrections based on steric considerations, resulting in better performance in some cases. The other difference is that the SAPRC SARs were re-optimized using the full set of available rate constants in our rate constant database (McGillen et al, 2020), while the MCM/GECKO-A SARs were developed

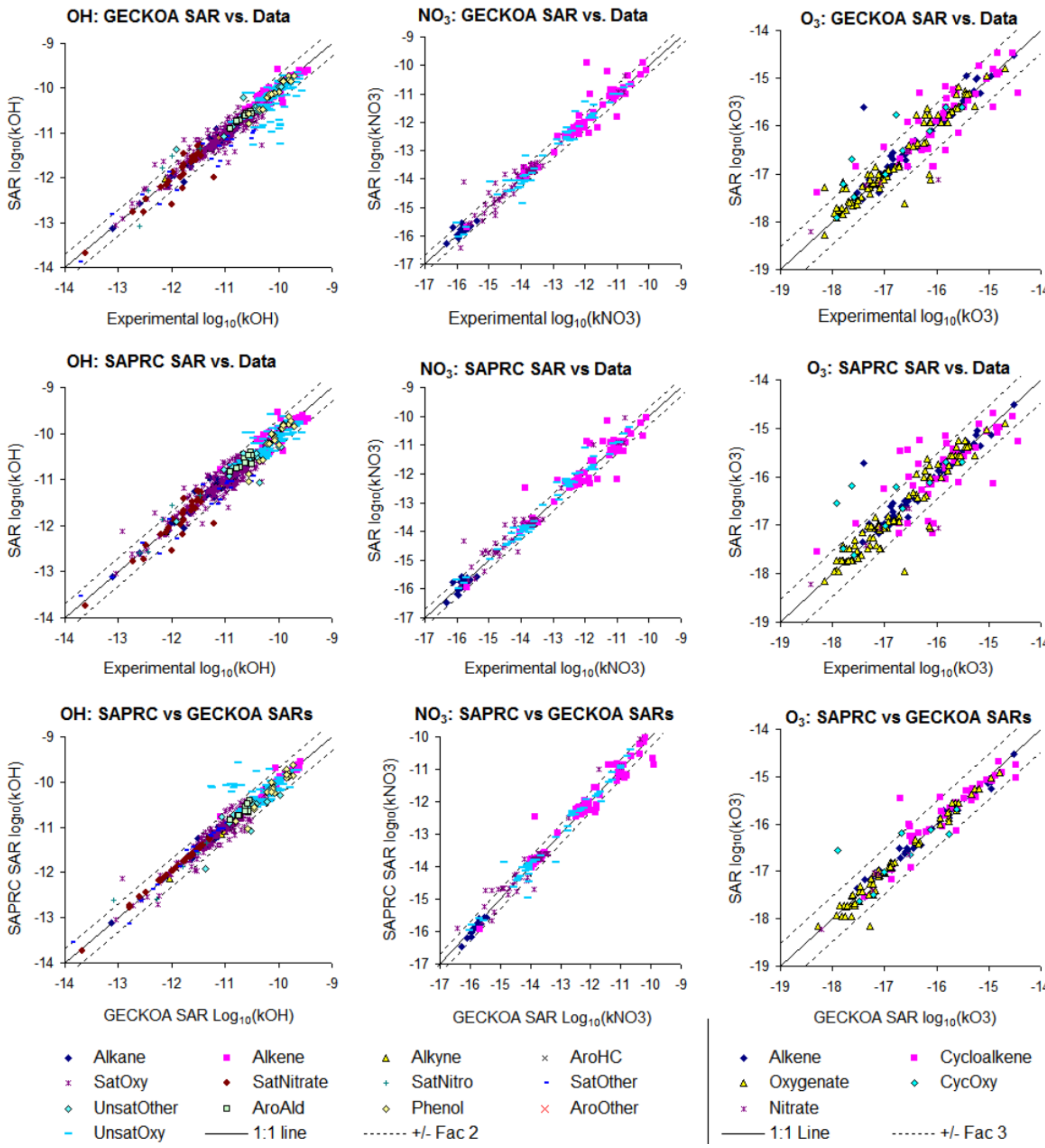
Table 11. Information and abstract of the latest draft of the "Site of Attack" database paper that is in preparation.

Title	The use of OH/VOC 'site-specific' rate coefficients and branching ratios to test and improve Structure – Reactivity Relationships
Authors	J. J. Orlando, W. P. L. Carter, M. R. McGillen, B.Aumont
Status	In preparation. Complete draft exists and is being reviewed by authors.
Abstract (draft)	The atmospheric removal of volatile organic compounds (VOCs) is predominantly initiated by their reaction with OH radicals, and thus the measurement and prediction of OH/VOC rate coefficients and branching ratios is of critical importance in the quantitative modeling of tropospheric chemistry. Rate coefficients (k) for OH/VOC reactions have been reported for about 1500 compounds, while the remainder are determined using structure-activity relationships (SARs). In general, these SARs predict not only the total k, but also branching ratios for the OH/VOC reaction– i.e., the percentage of reaction occurring at each unique site in the molecule. However, the veracity of these SAR-derived branching ratios has not been systematically evaluated. In this work, published data from environmental chamber studies of OH/VOC oxidation have been examined and 194 cases are found where a chamber study provides branching ratio information for an OH/VOC reaction. These retrieved branching ratios (or equivalently, 'site-specific' rate coefficients, kss) are compiled and used to test the accuracy of three OH/VOC SARs for VOCs categorized by functional group. The ability of the SARs to correctly predict branching ratios degrades with increasing functionality on the molecule (along the series alkanes, aldehydes and ketones, organic nitrates, ethers and alcohols, acids and esters, and multi-functional species), with mean absolute errors in the predicted branching ratios increasing from as low as 0.03 for the alkanes to 0.2 for esters and some multifunctional species. A similar trend is seen in the comparisons of SAR-determined kss data with those obtained from the chamber data. Specific cases where large disagreement exists between the SARs and chamber data are noted, and suggestions are made for either SAR improvement or for further experiment to resolve discrepancies.

before this database was available, using their own datasets. Note that the McGillen et al (2020) database was used for the SAR comparison in this work.

The SAPRC SARs were implemented into MechGen (Carter et al, 2025a,b), which was used to calculate the rate constants given the structures of the molecules and the values parameters used in the SARs. To allow comparisons for the same sets of compounds, including those not considered by Jenkin et al (2018a,b, 2020) or Kerdouci et al (2014), the updated GECKO-A SARs were also implemented as an option in MechGen, which was then used to calculate the GECKO-A SARs for the comparison. This was not straightforward in all cases because some of the GECKO-A SARs used steric corrections not used by SAPRC or implemented in MechGen, and these had to be programmed. The MechGen implementation was tested by comparing its predictions against those given in the MCM/GECKO-A SAR papers, and good agreement was obtained in all but a few cases. Fortunately, Jenkin (personal communication) was able to help us in resolving almost all of the disagreements, with the few remaining discrepancies being removed from the comparison.

Figure 2 shows the performance of the updated GECKO-A and SAPRC SARs in predicting the OH NO_3 and O_3 rate constants in the McGillen et al (2020) dataset, and also comparing their predictions against each other for the same compounds. Note that the compounds used are restricted to those that can be predicted using both sets of SARs, so is not the full set of compounds in the experimental dataset. The results show that both sets of SARs perform similarly in predicting the available data, though statistically the GECKO-A SARs perform somewhat better for OH and O_3, while the SAPRC SARs are slightly better for NO_3. As expected, the SARs perform the best and are most similar for the classes of compounds for which there are the most data.



(Rate constants are in units of cm^3 $molec^{-1}$ s^{-1})

Figure 2. Plots of SAR predictions, using two different methods, for rate constants for reactions of VOCs with OH NO_3 and O_3 against experimental data and against each other.

Note that the comparisons of the these SARs as shown on Figure 2 are not strictly speaking fair because the parameters in the SAPRC SARs were optimized to fit the experimental data used for the comparisons, while the updated GECKO-A SARs were developed using a subset of these data. It can be argued that a fairer comparison would be to optimize all SARs using exactly the same data. However, the facts that the SARs perform about the same for OH and NO_3, and that the GECKO-A SARs are somewhat better in some cases indicate that this is not a major factor. This is probably because the datasets used when developing the GECKO-A SARs were already reasonably comprehensive for the types of compounds covered by these SARs, with the McGillen et al (2020) dataset differing mainly in including data for reactions not covered by these SARs, and thus not relevant to this comparison. However, the more extensive dataset will allow extending these SARs to other classes of compounds.

2.8. Review of Treatment of Photolysis Reactions in Models

The objectives of the photolysis group are to review and make recommendations on treatments of photolysis reactions in mechanisms in models. Representing photolysis reactions requires making assignments or estimates for both absorption cross-sections of the various types of compounds where photolysis is important, and assigning or estimating the quantum yields, both of which in general are wavelength-dependent, and also sometimes dependent on temperature and pressure. This is a large task owing to the vast variety of multifunctional photoreactive species formed, most of which are represented in mechanisms using a much smaller number of lumped model species, and the experimental uncertainties and data limitations concerning quantum yields. It was decided that the first task would be to review how photolysis reactions are treated in current atmospheric mechanisms, to determine areas of uncertainty and highlight where priority improvements are needed.

The rate constants for photolysis reactions, or photolysis frequencies, depend on the intensity and spectrum of the photolyzing light (e.g., the actinic fluxes for ambient sunlight) as much as they do on the absorption cross-sections and quantum yields of these reactions. This means that they are properties of the environment being modeled as well as the chemical mechanism employed. To address the need to compare photolysis frequencies for the same conditions, the Tropospheric Ultraviolet and Visible (TUV)

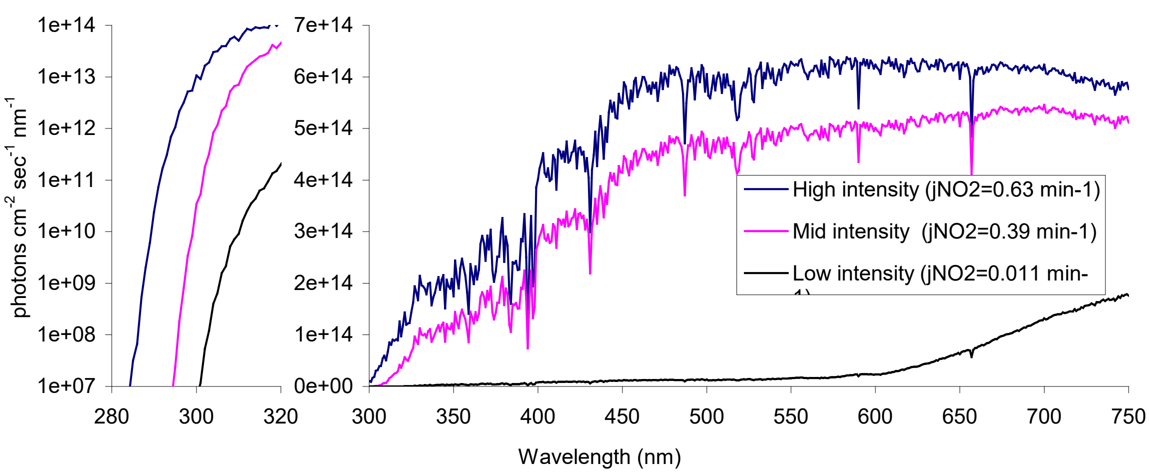


Figure 3. Plots of standard actinic fluxes used for comparison of photolysis rate calculations

radiation model (TUV, 2019) was used to develop three sets of actinic flux spectra representing high, mid, and low UV conditions, respectively. These were calculated using the TUV defaults except that the high intensity fluxes were calculated for a solar zenith angle of 0° (overhead sun) and ozone column of 200 Dobson units, the mid intensity fluxes were for zenith angle of 60º and 350 Dobson units, and the low intensity fluxes were for zenith angle of 90º and 500 Dobson units. Although these three do not reflect the full range of actinic fluxes and light intensities that may occur in the atmosphere, especially under high aerosol or overcast conditions, they are considered sufficient for elucidating the extent to which photolysis reactions predicted by different mechanisms differ under high, mid, and low UV conditions. These actinic fluxes so derived are shown on Figure 3.

For our initial comparisons, we obtained absorption cross section and quantum yield data used to calculate photolysis frequencies in a number of existing mechanisms, and using them to calculate photolysis frequencies with the standard sets of actinic fluxes discussed above. These mechanisms are listed in Table 12, which also indicates the source of the data used and calculation method for those mechanisms for which we have the necessary data. For comparison purposes, we also obtained photolysis frequencies calculated using the absorption cross section and quantum yield data used in the dataset included with the standard TUV model (TUV, 2019). The TUV photolysis frequencies are used as a mechanism-independent basis for comparisons of calculated photolysis frequencies.

Figure 4 shows the photolysis frequencies calculated using the absorption cross-sections and quantum yields available in the standard TUV model for the three standard actinic fluxes, ordered by magnitude, with the mid-intensity fluxes. The magnitudes for the high and mid intensity fluxes are very similar in most cases, though the differences increase for the slower photolysis reactions that tend to be most sensitive to the shorter wavelengths where the fluxes are most sensitive to changes in zenith angle or the ozone column. The relative differences in the photolysis frequencies calculated using the absorption cross-sections and quantum yields in the various mechanisms, compared to those using the standard TUV dataset, are shown in Figure 5. The reactions shown are restricted to those that are common to the mechanisms being compared, so they do not include all the photolysis reactions in the more detailed mechanisms such as MCM (2023) or SAPRC-22 (Carter, 2023), nor all the reactions in the standard TUV dataset. The discrepancies are shown for the mid-intensity fluxes for all reactions are also shown for the high and low intensity fluxes for the three reactions where the discrepancies were the greatest.

For most reactions, the calculated photolysis frequencies for the recent mechanisms (MCMv3.3, SAPRC-22, RACM2, and CB6) agreed to within ~15%, except for methyl glyoxal, organic nitrates for all fluxes, and $O_3 \rightarrow O(^1D)$ for the mid and low intensity fluxes. The greatest differences are for methyl glyoxal, suggesting that this needs to be examined when the mechanisms are updated. The differences for the lumped nitrate species may be a lumping issue, and may depend on what is used as the surrogate compound to derive absorption cross sections for the lumped model species. The differences for $O_3 \rightarrow O(^1D)$ at the mid and low intensity fluxes may be due the fact that RADM2/RACM2 assumes a faster rate of falloff in quantum yields with wavelength at above 312 nm than assumed in the TUV dataset and the other mechanisms. We have not yet assessed the extent to which these differences reflect use of outdated data on some mechanisms, different assumptions or conclusions drawn from current data by mechanism developers, or different lumping approaches.

As indicated above, this comparison does not cover all types of photolysis reactions, being restricted to only those that are comparable among all the mechanisms examined. The more detailed mechanisms employ more model species for some types of photoreactive species, and therefore can have different photolysis frequencies when representing compounds that are lumped together in the more condensed mechanisms. The effects of lumping these species in calculations of overall photolysis

Table 12. Summary of datasets or mechanisms or used for comparing photolysis frequencies.

Mechanism or dataset	Description and source of absorption cross section and quantum yield data and calculation method.
TUV (TUV, 2019)	The TUV model dataset includes absorption cross-sections and quantum yields for most photolysis reactions used in current mechanisms, so photolysis frequencies as well as actinic fluxes can be calculated. The TUV photolysis frequencies were those that were output by TUV when the standard actinic fluxes were calculated.
MCMv3.3.1 (MCM, 2023)	This is a semi-explicit mechanism that has 34 types of photolysis reactions, making it the most detailed of the mechanisms used in the current comparison. The photolysis frequencies for the standard actinic fluxes were calculated using the TUV model using absorption cross-section and quantum yields obtained from the MCM web site (MCM, 2020a).
SAPRC-22 (Carter, 2023)	This is the latest and most detailed version of the SAPRC mechanisms and has 38 types of photolysis reactions, somewhat more than MCM. The absorption cross-sections and quantum yields are available online at the SAPRC-22 web page (Carter, 2025a). The photolysis frequencies were calculated using the SAPRC modeling software (Carter, 2025b).
SAPRC-07 (Carter, 2010)	This is a moderately condensed mechanism with 29 types of photolysis reactions. The absorption cross-sections and quantum yields are given in the mechanism documentation and provided with the mechanism files that are available online (Carter, 2025b). The photolysis frequencies were calculated using SAPRC modeling software.
RADM2 (Stockwell et al, 1990)	This is a moderately condensed mechanism with 21 types of photolysis reactions. Files containing absorption cross-sections and quantum yields were previously provided to Carter as part of a collaborative project to evaluate the RADM-2 mechanism when it was initially developed (Carter and Lurmann, 1990). The photolysis frequencies were calculated using the SAPRC modeling software (Carter, 2025b).
RACM2 (Goliff et al, 2013)	This is the latest in the RACM/RACM series of mechanisms and has a similar level of condensation as RADM2. The absorption cross section and quantum yield data were provided by Stockwell (private communication), and the frequencies were calculated using TUV.
CB05 (Yarwood et al, 2005)	This is a highly condensed mechanism with 21 types of photolysis reactions. Files containing the absorption cross-sections were provided to Carter by Greg Yarwood (personal communication) shortly after that mechanism was published. The photolysis frequencies were calculated using the SAPRC software (Carter, 2025b).
CB6 (Yarwood et al, 2010)	This is an update to CB05 with a similar level of condensation. The absorption cross section and quantum yield data were provided by Yarwood (private communication), and the frequencies were calculated using TUV.

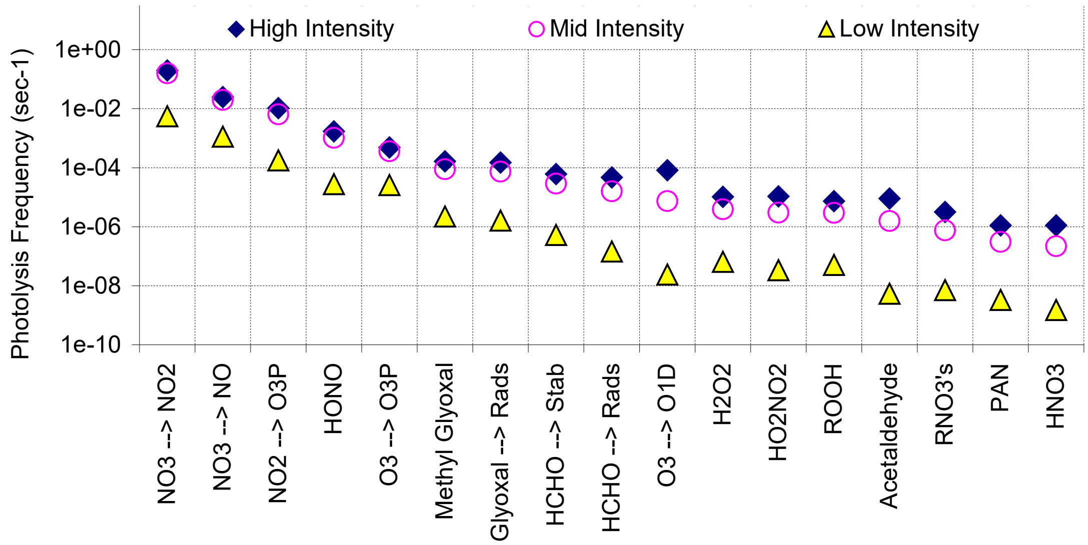


Figure 4. TUV-calculated photolysis frequencies used for mechanism comparisons, calculated for the three standard actinic fluxes.

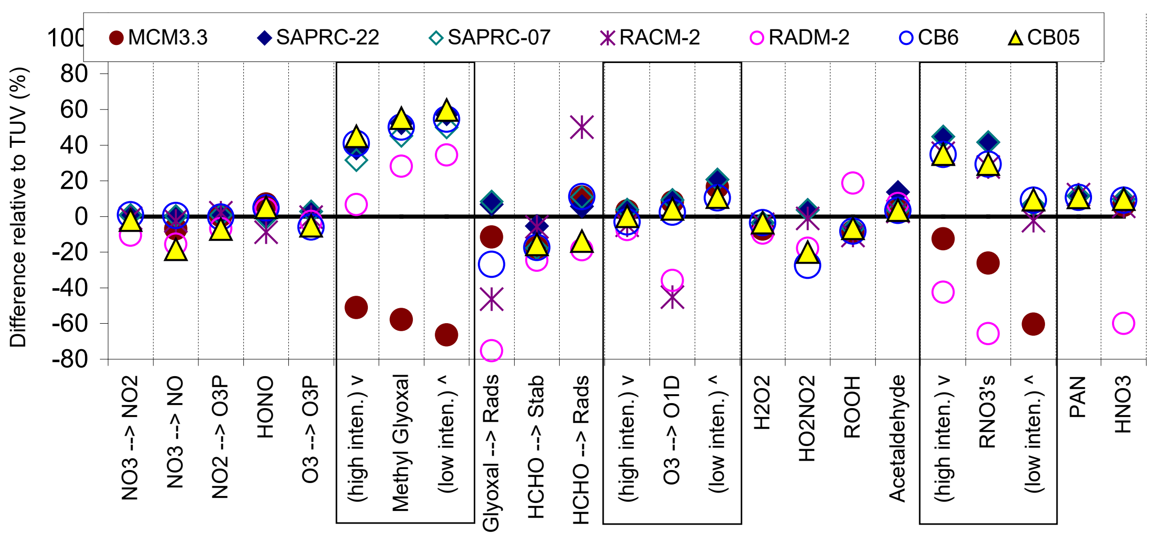


Figure 5. Relative differences in calculated photolysis frequencies for various mechanisms compared to standard TUV-calculated photolysis frequencies. These were calculated using the mid-intensity actinic fluxes unless indicated otherwise.

(Note that the relative differences shown were calculated as 100 * (J^{mech} - J^{TUV}) / average (J^{mech}, J^{TUV}), where J^{mech} are the photolysis frequencies calculated using the actinic fluxes and quantum yields used for the mechanism, and J^{TUV} are calculated using those in the standard TUV dataset.)

frequencies need to be assessed, especially for the most important multifunctional species. In addition, all the current mechanisms have highly photoreactive model species that represent the various highly photoreactive unsaturated aromatic ring-opening products, but the photolysis frequencies are not comparable among all mechanisms because of differences in yields and photolysis mechanisms of the model species representing these products. However, how the mechanisms represent the photolysis reactions of the photoreactive aromatic products are important in affecting predictions of aromatic reactivity, so we will need to derive methods to compare them that take differences in yields and radical input frequencies into account.

It is also known that photolysis frequencies calculated from absorption cross section, quantum yield, and actinic flux data can depend on the specific calculation methodology and the wavelength resolution of the data employed. As indicated in Table 12, the photolysis frequencies given here were calculated either using TUV methodology and software or using photolysis calculation software in the SAPRC modeling system (Carter, 2017). The reasonably good agreement between the SAPRC and MCM values for most of the reactions suggest that the SAPRC and TUV methodologies are not significantly different in practice, though this may not be the case for all methodologies used to derive photolysis frequencies for the different models. Comparisons of methodologies and evaluations of other issues such as wavelength resolution will be carried out as part of this study, and recommendations will be made on appropriate approaches for intercomparison studies and modeling.

2.9. Initial Work on SARs for Photolysis

A longer-term objective of our photolysis group has been to review SARs and estimates for photolysis reactions in atmospheric chemical mechanisms. A starting point is the set of photolysis estimates and SARs being developed for the update to MCM/GECKO-A in the draft report by Bräuer et al (2020), for which three of our members are co-authors. This discusses estimates for both absorption cross-sections and quantum yields for a wide variety of compounds that need to be represented in detailed mechanisms such as MCM, or predicted to be formed by mechanism generation systems. Our group was requested to review and comment on this report, and make recommendations.

Photolysis reactions depend on both absorption cross sections and quantum yields, so SARs for both need to be developed and evaluated. However, it was decided to focus initially on absorption cross sections, since developing SARs for quantum yields, though important, is a much more difficult problem and data are more limited. The initial focus was on aldehydes, and we collected available absorption cross data for various aldehydes. It was found that the compound-by-compound variability was such that it was unclear how to reliably estimate absorption cross sections for substituted aldehydes for which there are no data. It was decided that theoretical input is necessary for further progress.

Several group members were aware of the work of the group of Basile Curchod on theoretical calculation of photolysis reactions of atmospheric VOCs (e.g., Prilj et al, 2022), and we contacted him to see if we could collaborate on this problem. He was interested in this project, and several teleconferences where held involving our photolysis group and members of his work. Although the photolysis group became less active during the later period of this project, Curchod's group is still active in this area (e.g., Hollas and Curchod, 2024). The possibility of additional work in this area is discussed in Section 3.

2.10. Development of a Theoretically-Calculated Rate Constant Database

As with VOC SARs, it was decided to focus first on data gathering before working on reviewing SARs for radical reactions. However, experimental data on rate constants of radical reactions, especially for the wide variety of oxygenated or nitrogen-containing radicals formed in atmospheric reaction systems are highly limited, because direct experimental measurements of such reactions tend to be difficult to carry out or difficult to interpret unambiguously. Fortunately, quantum theory has reached the point where it provides a useful supplement to experimental data for evaluating SARs, especially for radical reactions where direct experimental measurements are difficult to carry out and are limited. However, despite their increasing importance, comprehensive compilations of theoretical data useful for SAR evaluations do not exist. Without such a compilation, it is difficult to develop and comprehensively evaluate SARs for radical reactions.

Therefore, it was decided early in this project to initially focus on compiling quantum calculation data on atmospheric reactions of organic radicals, to supplement the more limited experimental data. This effort was carried out primarily by Luc Vereecken of our group as a result of our discussions, and to support his ongoing research into developing radical SARs (see Table 4). The theoretical kinetics data base that Vereecken is developing is called "TheoKinDB. A flier describing the development of the database was distributed at the International Gas Kinetics (GK25) meeting in 2018 to make other theoretical chemists aware of this work and invite them to contribute.

Significant progress was made earlier in the program with regards to data input, software, documentation and database formulation. Unfortunately, progress subsequently slowed considerably due to lack of funding, and efforts were diverted to developing several theory-based SARs (see Table 4) though this The development of database is still remains a priority for SAR development, and the extensive theoretical data generated for the SARs is earmarked to be included. The possibility of additional work in this area is discussed in Section 3.

2.11. Other Projects

Additional items that were discussed during our teleconferences were keeping up to date on work on the various mechanisms and mechanism generation systems being developed or maintained by group members. Several members of our group are working on a collaborative project for an EPA-funded program to compare predictions by the MechGen and GECKO-A mechanism generation systems of products formed in multi-generation mechanisms of several representative compounds (Lee-Taylor et al, 2025 -- see Table 3) and some potentially significant differences were observed. Most of these differences are attributed to differences in radical SARs, which is an active area of research by our member Luc Vereecken, but which has not been a focus of this project because it was decided to wait until there is more progress in developing the theoretical kinetic database. The possibility of additional work in this area is discussed in Section 3.

Thermochemical estimates are important to mechanism development for assessing feasibilities of possible reactions and are used by some SARs. Because of this, we formed a Thermochemistry group to review available thermochemical estimation assignments and data and recommend data that should be used for SARs that need thermochemical estimates. The thermochemical group values used by the SAPRC and GECKO-A mechanism generation systems were compared, and significant differences were found. However, progress was slow and this effort was discontinued after members who are experts in photochemistry ended participation with our group.

3. DISCUSSION AND ONGOING WORK

Although the CRC-funded portion of this project has ended, there is a consensus among participants that this has been a useful collaboration for advancing detailed chemical mechanism development that should continue in some form. While the original objective has focused on reviewing and making recommendations on existing SARs, following extensive discussions it was determined that what was needed in the nearer term was making the research community aware of the needs and priorities for mechanism and SAR development, collecting data needed for SAR development and making them easily available online for this purpose, investigating new approaches for SAR development, and improving treatments of photolysis in estimated mechanisms and models. This resulted in two published papers on research needs, two papers (published and under review) on a new SAR approach for an important class of reactions, compiling and publishing an online database of measured rate constants reactions of VOCs with atmospheric oxidants, and beginning work on compiling other types of data needed for SAR development, and making some progress on treatments and estimates for photolyses.

This effort has proven to be sufficiently beneficial to the participants that they were willing to use volunteer or use their own funds to support their participation in this project. Travel expenses turned out to be less than initially estimated because online meetings and email exchanges were found to be sufficient in most cases for progress to be made. This has resulted in our being able to continue this CRC project for many more years than initially planned without additional funding. Based on this experience, we believe that the amount of funding needed to continue this collaboration into the future is relatively small. Of course, the collaborations may well result in development of proposals for work that would require separate funding, but this additional work could be carried out in coordination with this project.

The Principal Investigator of this project has made a donation personal funds to UCR to establish a fund for atmospheric chemical mechanism development research, and we will propose to use a portion of these funds support the administrative costs for continuing the work discussed in this report. This will include continuing to work on the following ongoing and unfinished projects discussed in Section 2.

- We are continuing collecting available published data on measurements of rate constants for reactions of organics with OH, NO_3, O_3, and Cl, discussed in Section 2.2, and expect to update our online database early next year. This data collection and periodic updates to this dataset will continue.
- Work on developing the E-state method for estimating VOC + OH rate constants, discussed in Sections 2.4 and 2.5 will continue, with the method being extended to other classes of compounds. The goal will be to have SARs that will cover the full class of compounds where estimates are needed for developing and generating detailed mechanisms. Comparisons different SARs for these types of reactions will be included as part of this effort.
- Work that we have started on collecting and making available experimental product yield data for developing and evaluating SARs is expected to continue. The manuscript on "site of attack" product data for VOC + OH reactions is expected to be submitted early next year, after which we will work on making these data available online in a useful form for SAR evaluation. We will then consider working on collecting and making available online product yield data relevant to branching ratios for radical reactions, such as reactions of peroxy radicals with NO, the many types of reactions of alkoxy radicals, and reactions of other types of intermediates. Work on how to use such data for SAR evaluation and development is also needed, since many of the experimental systems are complex and not straightforward to analyze.
- Although this effort has stalled in recent years, we hope to eventually complete a manuscript on our review and comparison of treatments of photolysis reactions in models, using the work discussed in Section 2.8 as a starting point. Strictly speaking this is more an issue of how

mechanisms are implemented in airshed models than mechanism development as such, but this is an important area that has not received adequate attention by mechanism developers and modelers, where a comprehensive review, evaluation, and recommendations are needed.

- We had attempted to start a review of estimates for photolysis reactions, focusing on initially on estimates of absorption cross sections. Our efforts were stalled until we realized we needed more input from theoretical chemists working in this area, so we initiated a collaboration with Basile Curchod to provide input in this area. This collaboration should help focus the theoretical work on priority areas for mechanism development. We hope that this collaboration can continue in some form.
- Although Vereecken's work on developing a theoretical kinetic database relevant to developing SARs for radical reactions has stalled because of insufficient funding, we hope that this work can be continued. Once this is completed sufficiently, we can begin considering evaluating or developing SARs for radical reactions, similar to our work on SARs for VOC + oxidant reactions.

Our group will continue discussion of other priorities for SAR and chemical mechanism review and development, and we may well initiate other projects and establish new goals. Additional funding will likely be needed to address some of these goals, and proposals for such projects will be developed as part of our work, to be funded by other sources but be carried out in coordination with our project. Our objectives will continue to be carry out work most needed to support development of comprehensive atmospheric chemical mechanisms that best reflect our evolving understanding of atmospheric chemistry.

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