SCIENCE AND TECHNOLOGY FOR ENERGY AND NATIONAL SECURITY

SAND2010-5889P

COMBUSTION RESEARCH FACILITY
SANDIA NATIONAL LABORATORIES / CALIFORNIA
CRF

July/August 2010 • VOL. 32, NO. 4

Engine combustion researchers develop laser absorption diagnostic to quantify in-cylinder CO

CRF researchers Russ Fitzgerald and Richard Steeper have recently developed an in-cylinder carbon monoxide (CO) sensor and tested it in their homogeneous-charge compression-ignition (HCCI) research engine. Because CO is an important indicator of hydrocarbon reaction progress, finding a new detection method is useful for studying many combustion phenomena, including engine combustion. In-cylinder measurements of CO can provide insight into the location and timing of CO production and consumption in the engine as well as contribute to the validation of chemical kinetic models of engine combustion.

Motivation for developing the new diagnostic arises from a current need to characterize combustion in prototype HCCI engines that employ a strategy called negative valve overlap (NVO). During NVO operation, residual gases are trapped and recompressed late in the engine cycle (see Figure 1), allowing a secondary injection of fuel that partially reacts during the NVO period. These NVO reactions can thermally and chemically affect the subsequent main combustion, thereby providing a rapid method of controlling the all-important main combustion phasing. A specific goal of the CO diagnostic work is to quantify the chemical reactions associated with NVO fueling.

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The multifaceted propene + OH reaction

The fate of unsaturated hydrocarbons is of general interest in both combustion and atmospheric chemistry. Propene (CH_3CHCH_2) is of particular interest as a prototype alkene fuel, as it may be expected to exhibit richer combustion chemistry than ethene (CH_2CH_2) and yet is simple enough to permit a detailed theoretical and experimental analysis. Propene is an important intermediate in almost all combustion mechanisms and can be also found in practical fuels.

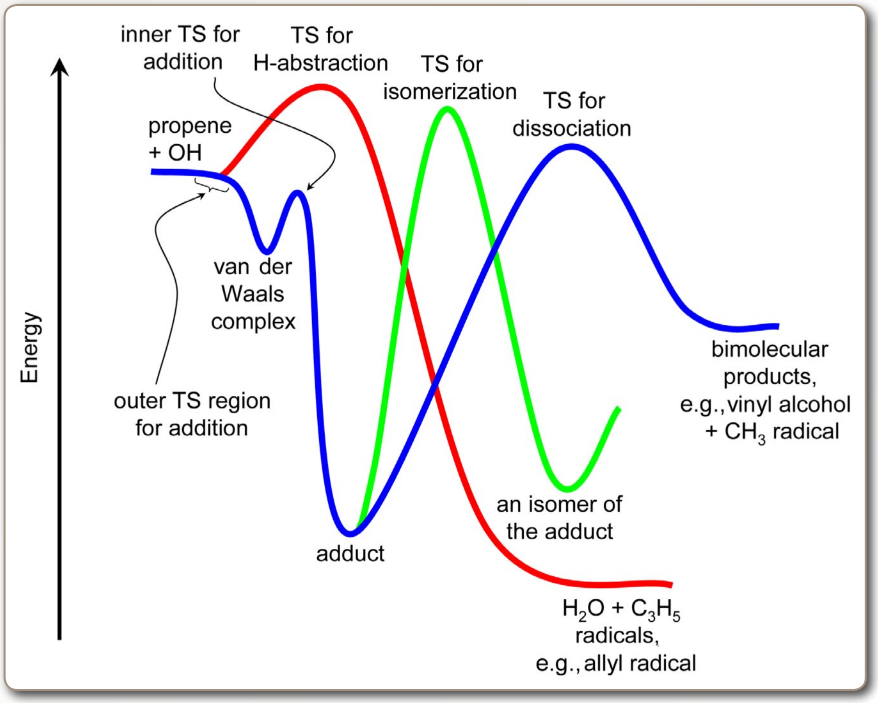

Figure 1. General features of the potential energy surface for the propene + OH reaction. TS: transition state.

The first step in propene oxidation is its reaction with OH:

$$CH_3CHCH_2 + OH \rightarrow \text{Products.}$$

Except at very low pressures, the major products below ~700 K are two adducts, $CH_3\dot{C}HCH_2OH$ and $CH_3CH(OH)\dot{C}H_2$. These radicals are identical to those formed from *n*- and *i*-propanol by H-atom abstraction on the β site (i.e., on the carbon atom adjacent to the hydroxyl functional group); therefore, the propene + OH reaction is intimately linked to low-temperature propanol combustion as well. It is crucial to know the rate coefficients of the above reactions across the entire relevant pressure and temperature range to evaluate both OH + propanol and bulk propanol combustion experiments. Describing propene and propanol combustion chemistry quantitatively is a critical step toward understanding biofuels combustion, because biofuels often contain both unsaturated and alcoholic molecular substructures.

The propene + OH reaction has been investigated experimentally for a very wide range of temperatures—50 K to 1250 K—by many research groups. Probably the most

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The multifaceted propene + OH reaction

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comprehensive set of data on this reaction in the temperature ranges relevant for combustion was measured at Sandia in the 1980s by Frank Tully. This data set was recently augmented by measurements over a wide pressure and temperature range in Craig Taatjes' combustion chemistry laboratory at the CRF and at the Karlsruhe Institute of Technology (KIT) in Germany. Both the overall rate coefficient and the product branching fractions of the propene + OH reaction are strongly temperature- and pressure-dependent, which makes this system particularly interesting and also challenging to study. In recent theoretical work, CRF researchers Judit Zádor, Ahren Jasper, and Jim Miller have provided a consistent description of the reaction, and supplied accurate rate coefficients to be used in combustion models (J. Zádor, A. W. Jasper, and J. A. Miller, *Phys. Chem. Chem. Phys.*, 2009, **11**, 11040–11053).

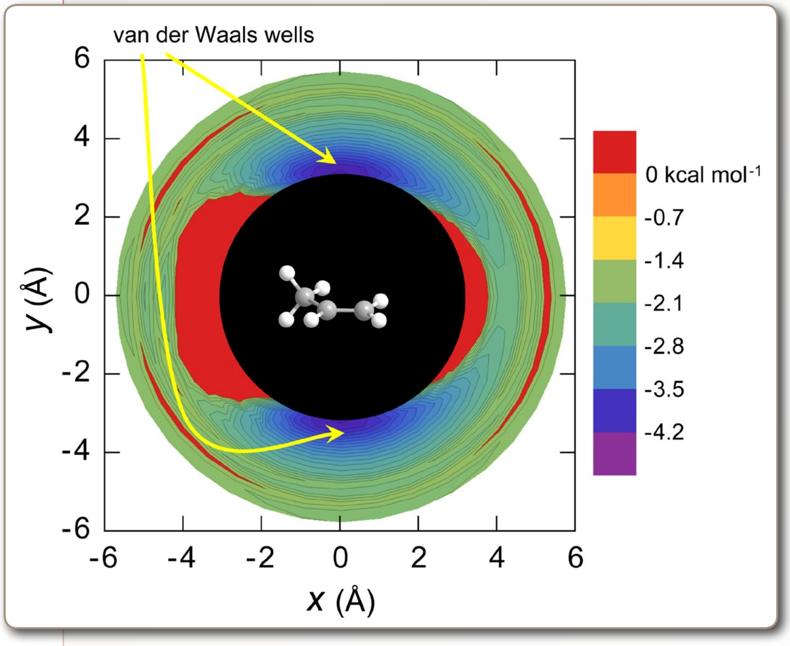

Figure 2. A 2D slice of the PES in the region of the outer transition state. Energies are calculated outside the black area only.

The complexity of the reaction arises due to the underlying potential energy surface (PES), which features ~50 stable intermediates, transition states, and possible bimolecular products. Molecular geometries and energies on this PES were determined using high-level quantum chemical methods, which provide enough accuracy to calculate reliable rate coefficients using transition state theory.

Figure 1 shows a simplified version of the high-dimensional PES that highlights its main features. The propene + OH reaction can proceed via a barrierless entrance channel to form a weakly bound van der Waals complex, followed by a small, submerged barrier leading to more strongly bound covalent adducts. At elevated temperatures these adducts can either dissociate back to the reactants, or can further isomerize by internal hydrogen-atom abstractions. Also, both the initial adducts and their isomers can dissociate to produce various bimolecular products. A very different pathway for the OH + propene reaction occurs when OH abstracts an H-atom directly and forms a water molecule next to an isomer of the $\dot{C}_3H_5$ radical.

The rate coefficient of the addition reaction is controlled by two transition states. The loose outer transition state is located at large intermolecular distances of the reactants, along the barrierless part of the potential (see Figures 1 and 2), and arises effectively due to centrifugal forces. The inner transition state is a more typical tight bottleneck; it is located at a smaller separation of the reactants and is associated with a saddle point on the PES. The overall flux through these two transition states is dictated by an inverse law, similarly to how the overall resistance of parallel resistances is calculated.

To calculate rate coefficients, the Master Equation (ME) methodology developed by Miller and Klippenstein was used. Their method essentially determines the governing time-scales of the chemical system's time-evolution by eigenvalue–eigenvector decomposition and rigorously finds time-scales belonging to chemical reactions, from which the phenomenological rate coefficients are derived. Transition state theory is implemented in the model using the rigid-rotor and harmonic-oscillator approximation in the framework of the Rice-Ramsperger-Kassel-Marcus (RRKM) theory. However, the number of states for the barrierless entrance channel has to be calculated variationally using direct variable-reaction-coordinate transition state theory (VRC-TST) to accurately account for anharmonicities associated with the looseness of the transition state in this region.

In accordance with the experiments (see Figure 3) addition was found to be dominant below ~500 K, and, in this temperature region, the rate coefficient has a negative temperature dependence due to the topography of the entrance channel. Above ~700 K, H-atom abstraction by OH is the dominant decay mechanism, as was observed experimentally as well. Abstraction shows a positive temperature dependence and readily leads to the formation of allyl radicals, one of the resonance-stabilized radicals that contribute to soot formation in flames. Addition continues to take place at these higher temperatures, but its importance diminishes

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PSI SUMMER INTERNS 2010

The annual summer intern program gives a high-tech twist to the age-old fall question: how did you spend your summer vacation? At the Physical Sciences Institute (PSI), high school, undergraduate, and graduate interns take physical-science problems "hands on." Working among top researchers in the CRF to develop ground-breaking diagnostic and remote sensing tools, PSI interns are immersed in a scientifically rich and dynamic research community, culminating in an end-of-summer symposium showcasing their projects. This summer's interns are (from left to right) Brittany Baker, Ramiro Becerra, Paul Nyholm, Nathan Greco, Peter Lillo, and Julia Wang. Information on Sandia National Laboratories' intern program can be found at ***http://sandia.gov/careers/stu-interns.html.***

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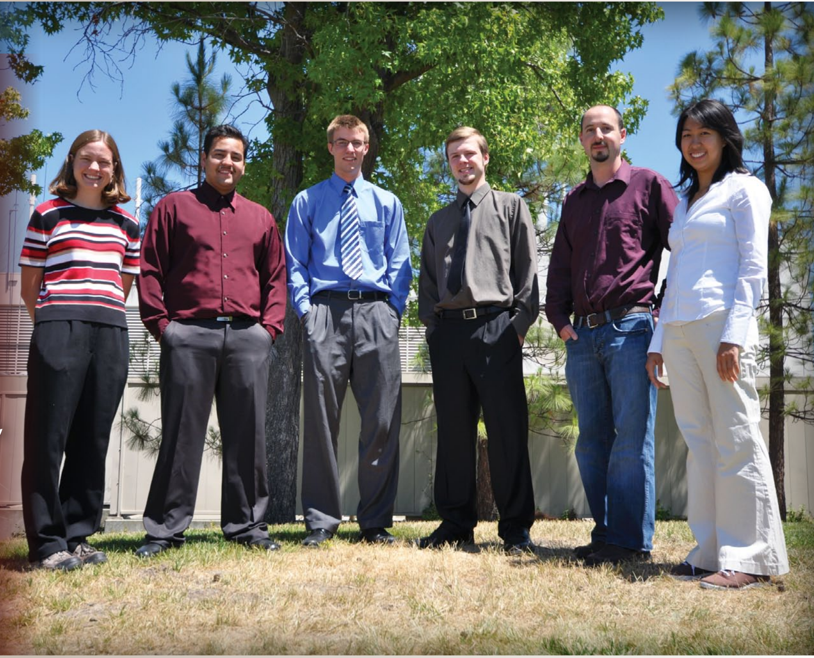


Intern team summer celebration

On July 15, CRF and Transportation Energy Center employees, interns, contractors, visitors, and their families (as well as more than a few pets) converged on Lake Del Valle near Livermore after work for the center's annual summer celebration. Back by popular demand, Cabana Dave's served up a flavorful Caribbean-themed barbecue.

Guests enjoyed breaking the ice and getting to know each other with activities such as volleyball, water-balloon catch, and an impromptu soccer match. (To everyone's relief, no vuvuzelas were on hand.)

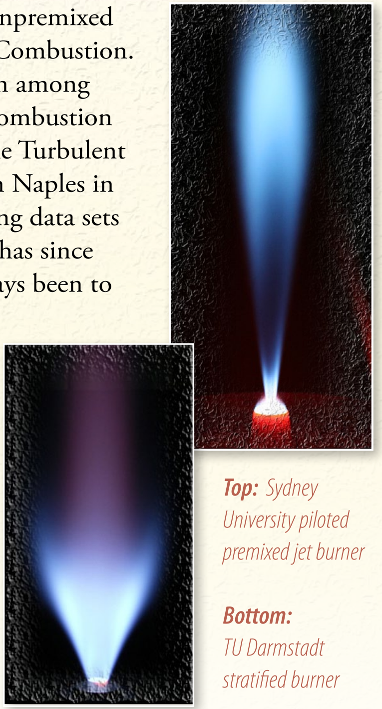
TENTH INTERNATIONAL WORKSHOP ON MEASUREMENT AND COMPUTATION OF TURBULENT (NON)PREMIXED FLAMES

TNF10 workshop 2010

TSINGHUA UNIVERSITY, BEIJING, CHINA • JULY 29–31, 2010

On July 29–31, the 10th International Workshop on Measurement and Computation of Turbulent Nonpremixed Flames was held at Tsinghua University in Beijing, just prior to the 33rd International Symposium on Combustion. The workshop—attended by 93 people from 13 countries—marked a decade and a half of collaboration among experimental and computations researchers to accelerate the development and validation of turbulent combustion models. Rob Barlow of the CRF's Reacting Flow Research department has been the lead organizer of the Turbulent Nonpremixed Flames (TNF) workshop series since its inception. The inaugural TNF workshop, held in Naples in 1996, established ground rules for comparison of measured and models results and selected a few existing data sets on simple hydrogen jet flames as targets for the first round of comparisons. The library of target flames has since grown to include greater complexity of flow fields and chemical kinetics, but the central theme has always been to understand and accurately predict the effects of turbulence–chemistry interaction in flames.

TNF10 marked an expansion of the scope of this collaborative endeavor to include target flames for a broader range of combustion modes: nonpremixed, partially premixed, stratified, and premixed combustion. The photographs at right show premixed and stratified burners that were added as new modeling targets for this workshop. The objective of this expansion is to contribute toward the development and validation of models capable of predicting the performance of practical systems that may operate across multiple combustion modes and regimes.



Top: *Sydney University piloted premixed jet burner*

Bottom:
TU Darmstadt stratified burner

Coordinators of the main sessions included J-Y Chen (UC Berkeley), Matt Dunn and Ed Richardson (Sandia), Andreas Dreizler (TU Darmstadt), Rob Gordon and Simone Hochgreb (University of Cambridge), Andreas Kempf and Peter Lindstedt (Imperial College), Ed Knudsen (Stanford), Heinz Pitsch (RWTH Aachen/Stanford), and Dirk Roekaerts (TU Delft).

"The success of the TNF series as a forum for international collaborative research is due to the willingness of key contributors to look beyond their individual research programs and invest significant time on work that has collective benefits. Coordinators of the sessions comparing measured and modeled results deserve special recognition," says Rob. Additional information on the TNF workshop series is available at *http://www.sandia.gov/TNF*.

CRF Adams & Bastress Award winners

On July 15, four CRF staff members were honored via the 2010 Adams and Bastress Awards. The O.W. Adams Award, named after Bill Adams, the U.S. Department of Energy's (DOE) original CRF sponsor, was established in 1986 and is given each year to Sandians who have made exemplary research contributions. This year's awards were presented to Nils Hansen, Paul Fugazzi, and Craig Taatjes from the Combustion Chemistry department for their recent contributions to understanding combustion chemistry using flame-sampling molecular-beam mass spectrometry. Exciting advances in this area have been made by employing tunable vacuum-ultraviolet photoionization at the Advanced Light Source of the Lawrence Berkeley National Laboratory.

Dedicated to the memory of Dr. E. Karl Bastress, who guided early combustion research activities for the DOE, the Bastress Award recognizes Sandians whose exceptional contributions have led to a strong and effective coupling of conservation-related programs to the needs of U.S. industry. The 2010 Bastress Award was given to Chuck Mueller for leading more than a decade of productive collaboration with Caterpillar as well as his significant contributions in biofuels research.

Laser absorption diagnostic to quantify in-cylinder CO

(Continued from page 1)

The approach adopted for CO detection in this work is absorption of infrared light (2.319-μm wavelength) from a tunable diode laser (TDL). Figure 2 demonstrates the multi-pass arrangement of the TDL system—the layout provides a long absorption path as well as a sample volume that covers a representative portion of a plane through the engine cylinder. A combination of flat and concave mirrors compensates for the beam-spreading effect of the quartz cylinder and finally focuses the beam onto a high-speed IR detector. To reduce noise generated by unavoidable particle scattering, window fouling, and beam steering in the optical engine, a wavelength modulation spectroscopy (WMS) technique was adopted. WMS makes use of the ability to modulate the diode-laser wavelength at high frequencies in order to tune out many lower-frequency noise sources, resulting in a significantly enhanced signal-to-noise ratio.

Following development and optimization of the diagnostic on the bench, the system was recently coupled to the optical engine. Initial tests were performed while seeding the intake air with CO during motored operation. Typical seeded-CO measurements are graphed in Figure 3 along with a motored pressure trace to orient the data with respect to cycle events. (The crank-angle axis has been shifted from Figure 1 to facilitate analysis.) The data points comprise 1-ms measurements recorded throughout the cycle and ensemble-averaged over 50 cycles. The gap in the data near TDC is due to beam obscuration by the piston and signal degradation at high pressures.

CO mole fraction during seeded operation theoretically should be both homogeneous and constant, and overall, the TDL data in Figure 3 are reasonably flat. From mid-intake stroke (halfway between intake valve opening and closing, IVO and IVC) to the TDC gap, the CO data accurately agree with the CO concentration determined from the metered flows of CO and intake air (4670 ppm). Similarly, following the mid-point of exhaust, the TDL data closely match CO measurements recorded using an emissions-bench CO instrument (4700 ppm). There are, however, a couple of anomalous dips in the CO data occurring near the time of intake and exhaust valve opening (IVO and EVO). High in-cylinder gas velocities are expected due to blowdown at these cycle times, but a connection with the anomalous CO measurements has not yet been established.

Tests of the new diagnostic have also been performed during fired operation. Sample CO data along with a fired pressure trace are illustrated in Figure 4 for a low-load operating point. In this fired case, the source of CO is incomplete combustion, and the data indicate large variations in CO concentration during the cycle. Just prior to IVO, CO rises rapidly due to NVO fuel reaction, and then falls as intake air mixes with cylinder contents. Mixing seems to be complete by the time of IVC, and, using this steady CO concentration along with an estimate of cycle residual gas fraction (RGF ~ 50%), a theoretical value of CO at IVO can be back-calculated. As indicated in Figure 4, this value agrees well with the local peak CO concentration measured by the TDL diagnostic. Following TDC, some variations in CO concentration occur that are not yet understood, but during exhaust (specifically, from 180 to 250 crank angle degrees), concentration is steady and, again, the data are consistent with the emissions bench measurement. These encouraging results suggest that the TDL diagnostic can provide reliable data to help characterize the role of NVO reactions during HCCI engine operation.

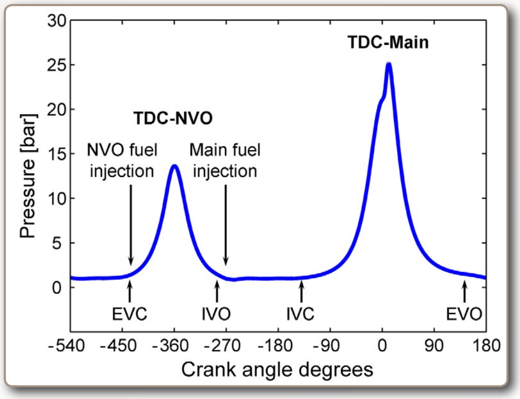


Figure 1. *Typical low-load HCCI-NVO pressure trace with top dead center (TDC) indicated for both NVO and main portions of the cycle. Labels at the bottom of the graph indicate the timing of exhaust valve and intake valve openings and closings.*

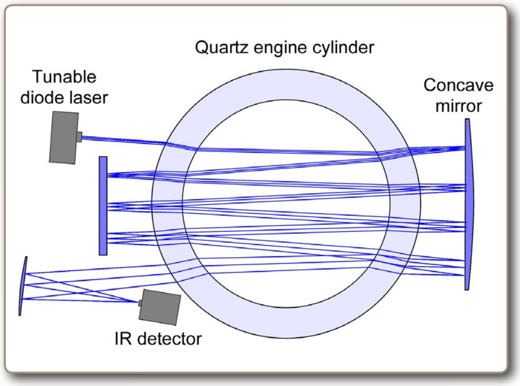


Figure 2. *TDL absorption diagnostic configured for in-cylinder measurement of CO.*

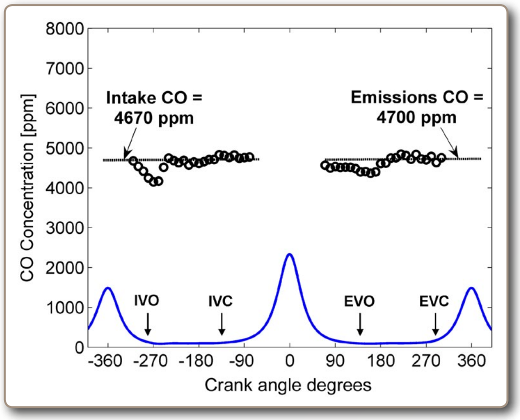


Figure 3. *Measured in-cylinder CO concentration (black circles) for a motored test seeded with 4670 ppm of CO. The data points represent 50-cycle ensemble averages. Dashed horizontal lines indicate independent measurements of intake CO and emissions CO. In-cylinder pressure (blue line) is superimposed for reference.*

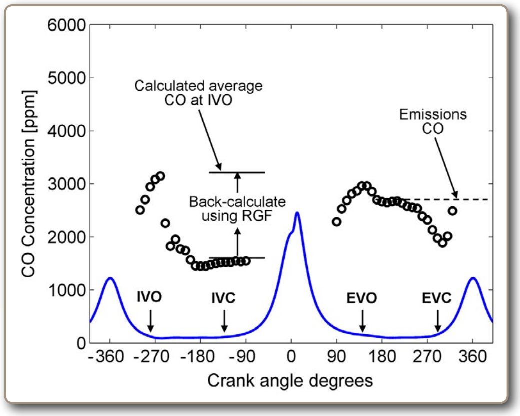


Figure 4. *Fired cycle CO measurements (black circles) for a test with 8.0 mg of main fuel (iso-octane) injected just after IVO and 1.3 mg of NVO fuel injected soon after EVC. CO data points represent 50-cycle ensemble averages.*

The multifaceted propene + OH reaction

(Continued from page 2)

due to fast backdissociation of the adducts to reactants. A fraction of the reactants forms non-abstraction bimolecular products. One important such product is vinyl alcohol, recently receiving a great deal of attention in combustion systems. Above 1000 K ~5% branching into vinyl alcohol is predicted, necessitating the inclusion of this reaction in comprehensive combustion mechanism.

Between ~500 and ~700 K addition, backdissociation, and abstraction are all important. In this temperature range the analysis of any experimental data must include the complex interaction of these processes. Our calculated rate coefficients were successfully used to model the newest CRF lab and KIT experiments, giving further evidence for the predictive power of these calculations.

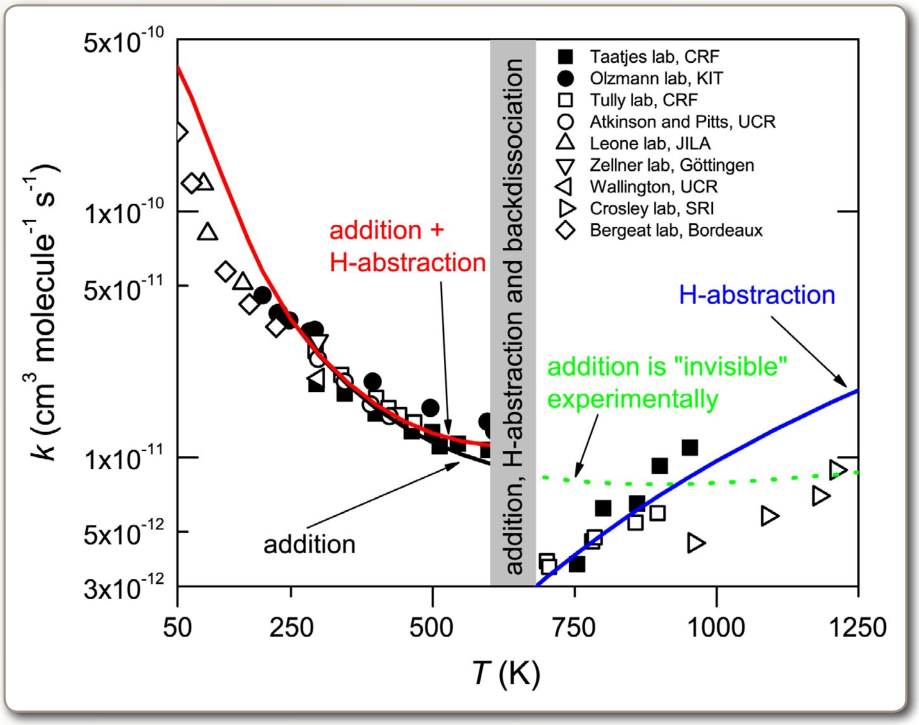


Figure 3. Calculated (lines) and experimental (symbols) rate coefficients at the high-pressure limit. In the grey region the rate coefficients can only be determined from the experiments by modeling the complex interaction of addition, H-atom abstraction, and backdissociation. Above ~700 K the fast backdissociation masks the addition process.

Further research is ongoing to continue to develop the model for the combustion of the *n*- and *i*-propanol isomers, largely based on these propene + OH calculations. Pressure- and temperature-dependent product branching fractions and unimolecular decomposition rate coefficients determine the initial radical pool present during propanol combustion, and they have a fundamental influence on bulk properties such as ignition delay times. Describing propene and propanol combustion chemistry quantitatively is a critical step toward understanding biofuels combustion, because biofuels often contain both unsaturated and alcoholic molecular substructures.

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ISSN 1548-4300

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