Frequency-Modulation Spectroscopy Characterizes R + O_2 Reaction Kinetics

Reactions of alkyl radicals with molecular oxygen are important steps in low-temperature combustion, autoignition, and engine knock. At low temperatures the reaction of an alkyl radical, R, with O_2 forms mainly the stabilized RO_2 adduct. As the temperature increases, HO_2 and a conjugate alkene begin to dominate; at temperatures of ~ 600 K, there is a transition region where the HO_2 yield dramatically increases. For the C_2H_5 + O_2 reaction (CRF News May/June 1999, Sept./Oct. 2000) theory and experiment provide a detailed understanding of the competition between stabilization and HO_2 elimination. In work supported by the DOE Office of Basic Energy Sciences, Craig Taatjes and John DeSain have investigated product formation in reactions of successively larger alkyl radicals with O_2, with the aim of building a detailed understanding of the reaction mechanism in the transition temperature region (575–700 K).

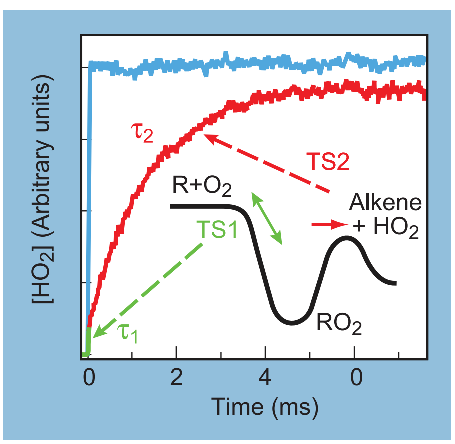


Figure 1. The observed HO_2 production (green and red trace) when cyclopentyl radical reacts with oxygen at 638 K can be explained by the simplified schematic of the potential energy surface (black line). The green section with time constant τ_1 is governed by the initial RO_2 formation (via the transition state TS1), while the red section, with time constant τ_2, is sensitive to the transition state for HO_2 elimination (TS2). The blue line is a plot of the reaction of CH_2OH + O_2 and represents 100% HO_2 yield.

In these experiments, alkyl radicals are formed from alkanes by hydrogen abstraction by photolytically produced Cl atoms. The progress of the reaction is monitored in time by continuous wave (cw) infrared frequency-modulation spectroscopy of the HO_2 product. In the transition temperature region, production of HO_2 occurs in two distinct steps. In the ethyl + O_2 reaction, it has been shown that the faster step is most sensitive to the transition state for addition, and the slower step to the transition state for HO_2 elimination, which lies ~ 4 kcal mol^{-1} lower than the reactants (Figure 1). The measurements of HO_2 production in reactions of larger alkyl radicals with O_2 will help determine whether the thoroughly studied ethyl + O_2 mechanism has more general applicability.

In reactions of ethyl, propyl, butyl, and cyclopentyl radicals with O_2, the total HO_2 yield rises sharply to nearly 100% between 575 and 675 K. The rate of HO_2 production differs for the various alkyl radicals investigated, but the effective activation energy for HO_2 production is remarkably similar for all the alkyl + O_2 reactions measured (Figure 2). This strongly suggests that a concerted elimination reaction from an initial RO_2 adduct is a common mechanism for HO_2 production. In all these reactions, the transition state is slightly lower in energy than the reactants. For the reaction of the larger alkyl radicals at higher temperatures, isomerization of the RO_2 adduct, resulting in formation of OH, can compete with HO_2 formation. Further investigations are underway to characterize these isomerization channels.

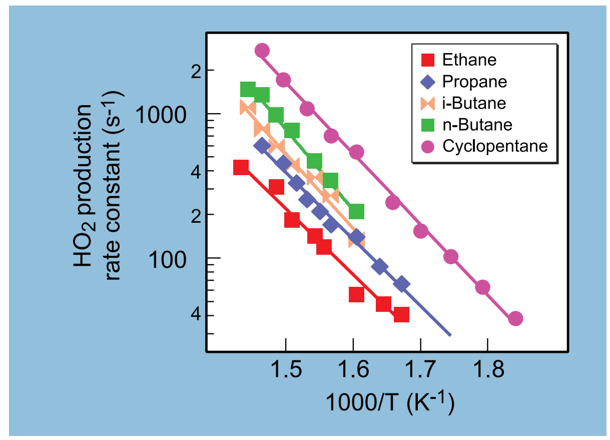
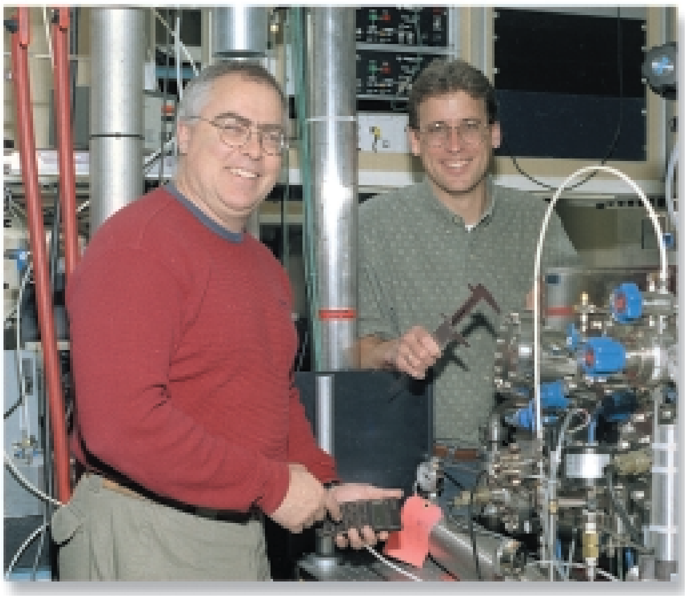


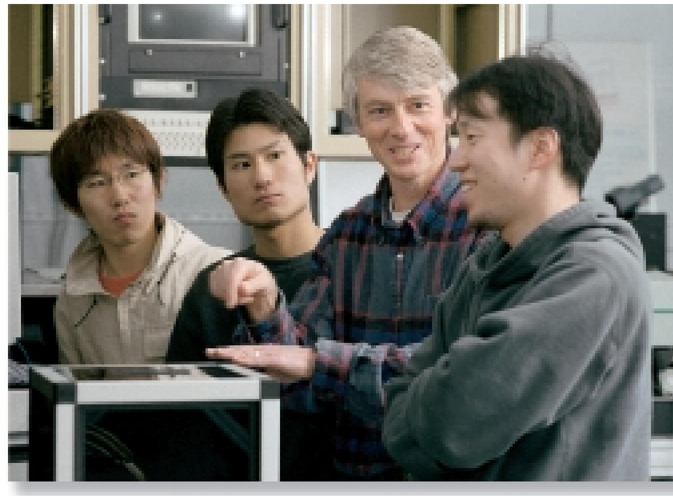
Figure 2. Arrhenius plots of the temperature dependence of elimination rate constants (i.e., $1/\tau_2$) for several different alkyl + O_2 reactions. The activation energy given by the slope of the lines is remarkably similar for all the reactions, suggesting similar energetics for HO_2 elimination.

People



Thomas Lorenz (right), who worked with David Chandler as a Limited Term Employee in the Chemical Dynamics Visitor Laboratory, recently took a permanent job at Lawrence Livermore National Laboratory (LLNL). During his 3 years at Sandia, Thomas worked on photochemistry and rotationally inelastic bimolecular collision dynamics using ion-imaging techniques. At LLNL, he will be working in the areas of laser and plasma physics.

Bassam Dally (center), from the University of Adelaide, Australia, visited Adonios Karpetis (left) and Rob Barlow to collaborate on experiments involving combustion in medium-temperature, reduced-oxygen environments, which produce very low levels of nitric oxide.



Shinichi Amano, Masaki Matani, and Jun Kojima (left to right), all students of Professor Yuji Ikeda of Kobe University in Japan, visited the three laboratories of the Reacting Flow Research Department to perform exploratory chemiluminescence measurements on several types of flames. Here they discuss experiments on turbulent pilot jet flames with Rob Barlow in the new Turbulent Combustion Laboratory.

Events

Rich Behrens describes his work on the decomposition of energetic compounds to members of the CRF Advisory Board, who were at the CRF for their annual program review, November 3–4. Pictured from left to right are Board Members Pat Flynn of Cummins Engine, John Stringer of EPRI, and Professors Ed Law of Princeton and Ron Hanson of Stanford. Not pictured is Advisory Board Member Professor Gregory McRae of MIT.

Glow-Plug-Assisted Ignition and Combustion of Methanol Studied in a Direct-Injection Diesel Engine

Studies of glow-plug-assisted methanol ignition and combustion at the CRF's Alternative Fuels Laboratory show that methanol fuel can produce thermal efficiencies comparable to conventional diesel fuel while producing significantly less in-cylinder soot and engine noise. Interest in methanol as an alternative fuel stems from longstanding concerns over the stability of petroleum supplies and the search for oxygenated fuels to reduce soot emissions from heavy-duty diesel engines. Methanol is a compelling choice for study because it represents an upper limit on the degree to which a fuel can be oxygenated. Furthermore, its thermophysical properties are vastly different from diesel fuel, and its in-cylinder combustion processes have not been well understood.

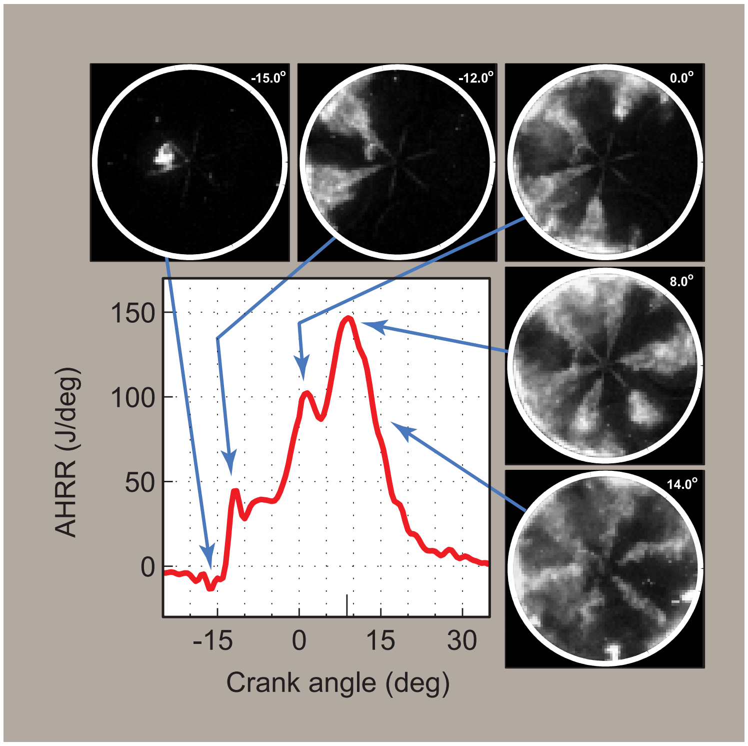


Figure 1. Conceptual picture of glow-plug-assisted methanol combustion. Pair-wise jet ignition events observed in direct luminosity (DL) images correspond to peaks in apparent heat-release rate (AHRR). Injection ends at 9 deg. Fuel jets emanating from injector are visible in first four images due to elastic scattering of DL from liquid fuel droplets.

One significant difference between methanol and a typical diesel fuel is that methanol does not autoignite at conditions where diesel fuel does. Ignition on a hot surface via a protruding glow plug is the most promising strategy for using methanol in compression-ignition engines. Chuck Mueller and Mark Musculus have studied glow-plug-assisted ignition of methanol in a four-stroke, heavy-duty, compression-ignition direct-injection (CIDI) engine, modified to provide extensive optical access to the combustion chamber. They gathered sequences of luminosity images and coupled them with thermodynamic analyses to compare the ignition and combustion characteristics of methanol and CN45, a paraffinic diesel reference fuel (65% heptamethylnonane and 35% n-hexadecane). They found that both proper glow-plug temperature and proximity to a fuel jet are critically important for smooth engine operation when methanol fuel is used. Once the glow plug is properly oriented with respect to the axis of the closest fuel spray, very stable engine power output can be achieved at charge temperatures typical of current heavy-duty diesel engines. Methanol ignition occurs at the glow plug, as expected, and combustion spreads to the two jets that straddle the glow plug. Combustion then "jumps" to adjacent pairs of jets as it makes its way to the side of the combustion chamber opposite the glow plug. They also found that each pair-wise jet ignition observed in the methanol image sequence correlated with a spike in the apparent heat-release-rate profile (see Figure 1).

In comparing the two fuels they found that in-cylinder soot levels were at least two orders of magnitude less for methanol than for CN45. Measurements of the engine work output and of the quantity of fuel injected for methanol and CN45 showed that the combustion efficiency of methanol is approximately equal to that of CN45 at the 1200 rpm, moderate load condition that was studied. In addition, peak heat release rates during methanol combustion were half those of CN45, resulting in noticeably quieter engine operation.

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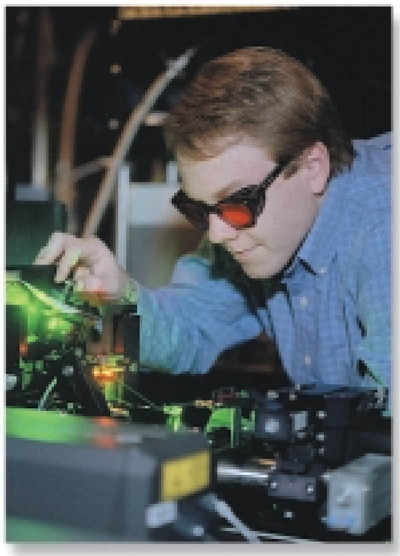

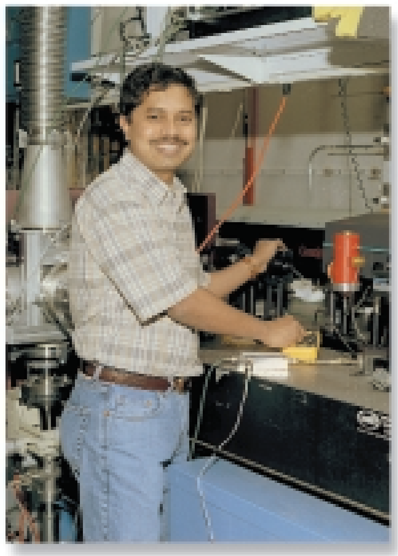

Adam Steeves (l), a student from Williams College, recently spent a month working with Andrew McIlroy in the Flame Chemistry and Diagnostics Laboratory investigating the application of continuous-wave cavity-ringdown spectroscopy for combustion species measurements. Initial experiments focused on the detection of oxygen in the near infrared using a Ti-sapphire laser. Also working with Andrew, are Sukesh Roy (r) and Prof. Bob Lucht (not shown) from Texas A&M University. They are investigating the use of infrared polarization spectroscopy as a combustion diagnostic. Proof-of-principle experiments have been carried out using carbon dioxide in an atmospheric pressure jet and a low-pressure cell.

As the new Visitor Program Administrator, April Cunningham will be responsible for a host of activities involving the many visitors to the CRF. Among her jobs are coordinating visits of foreign nationals and handling housing for short-term visitors and arrangements for no-fee visitors

Awards

Martin Summerfield

Rich Behrens recently received the Martin Summerfield Best Paper Award at the 5th International Symposium on Special Topics in Chemical Propulsion for his paper, "Chemical and Physical Processes that Control the Thermal Decomposition of RDX and HMX." Co-authored with Sandia Post-Doctoral Associate, Sean Maharrey, the paper describes experiments aimed at gaining further understanding of the chemical and physical processes that control the thermal decomposition of RDX and HMX.

Arch Colwell

John Dec has won his second Arch Colwell award in a row (1998 and 1999) for his paper, "Diesel Combustion: An Integrated View Combining Laser Diagnostics, Chemical Kinetics, and Empirical Validation." The Arch Colwell Award recognizes authors of outstanding papers presented at SAE meetings. John's paper was one of 14 selected for the award from over 2160 papers published for SAE meetings during 1999.

SAE Oral Presentations

Bob Green and John Dec received "Excellence in Oral Presentation" awards from the Society of Automotive Engineers (SAE) for presentations given at SAE meetings. Bob earned his award for a paper entitled "Measuring the Cylinder-to-Cylinder EGR Distribution in the Intake of a Diesel Engine During Transient Operation" given at the 2000 SAE International Fall Fuels & Lubricants Meeting & Exposition, October 16-19, 2000. John's award was for his paper "The Effects of Injection Timing and Diluent Addition on Late-Combustion Soot Burnout in a DI Diesel Engine Based on Simultaneous 2-D imaging of OH and Soot" presented at the SAE 2000 World Congress, March 6-9, 2000.

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Director: William J. McLean
Mail Stop 9054

Editor: Howard Lentzner
Email: hllentz@sandia.gov
Designer: Norma Calderon-Zablocki

Laser-Based Sensor Successfully Monitors Combustion Gases in Electric Arc Steelmaking

Optical sensors offer commercial steelmakers the possibility of real-time process control in high-temperature, high-velocity, particle-laden streams by means of remote, noncontacting measurements. In previous work funded by the American Iron and Steel Institute and DOE's Office of Industrial Technologies, Sandia demonstrated an optical sensor for the in situ, real-time measurement of off-gas composition and temperature during basic oxygen furnace (BOF) steelmaking. This work has now been extended to electric arc furnace (EAF) steelmaking by developing an instrument to provide real-time measurement of CO, CO_2, and H_2O concentrations and average line-of-sight gas temperatures in the EAF off-gas. Such an instrument will be invaluable for controlling and optimizing post-combustion and foaming slag practices, addressing industry needs for improved energy efficiency and emissions control, and developing automated process controls.

The optical sensor developed for steelmaking applications is based on mid-infrared tunable diode lasers (TDLs). Being noninvasive, the optical sensor is robust, relatively maintenance-free, and useful for characterizing off-gas streams in general. In collaboration with Robert Kolarik and Tom Webb (The Timken Company) and Gary Hubbard (Hubbard Associates), Sandians Sarah Allendorf, David Ottesen, Ben Chorpening, Doug Scott, and Allen Salmi recently completed a week-long test of the TDL sensor at The Timken Company's Faircrest Plant in Canton, OH.

Despite the harsh operating environment at this commercial steelmaking plant (immense electrical fields, occluded field of view, very limited access to equipment), sensor installation went smoothly, and the tests were a complete success. The sensor proved able to gather high-quality spectroscopic data through the off-gas in the air-gap between the elbow and drop-out chamber of an electric arc furnace (see Figure 1), and the team gained valuable experience in operating a TDL system in an industrial electric arc furnace setting. A photograph of a typical EAF shop is shown in Figure 2.

The sensor equipment was installed, aligned, and tested during a 30-hour furnace downturn. The TDL sensor successfully began acquiring off-gas data at the initial furnace startup. Overall, signal strength was very good and considerably exceeded expectations during stable, flat-bath operating conditions. Typically, signal levels were lowest during periods of scrap meltdown, presumably because of high dust levels generated during this portion of a melt. Electrical noise did not prove to be a problem, because of the careful layout of the system electronics and signal paths.

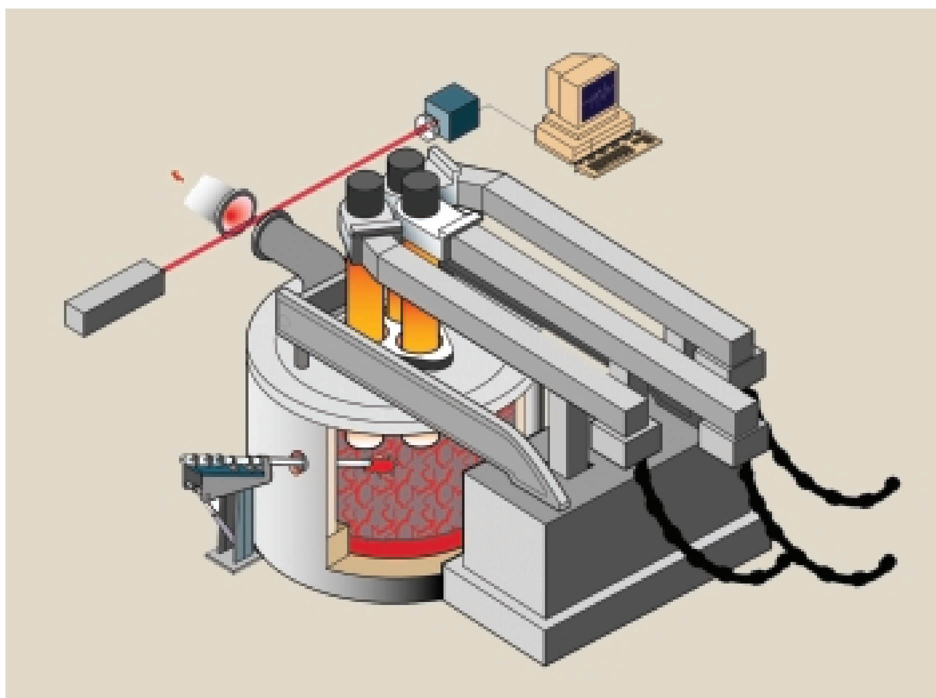

Figure 1. Schematic of the Sandia laser-based sensor installed on an electric arc furnace of the type used at The Timken Company's Faircrest Plant in Canton, Ohio. The mid-infrared tunable diode laser beam is transmitted through the off-gas in the air gap between the elbow and dropout chamber of the furnace and provides real-time spectroscopic measurements of CO, CO_2, and H_2O concentrations as well as gas temperatures.

Figure 2. A heat in progress at Timken's Faircrest Plant furnace. Visible emission from high temperature gases and particles is seen through the furnace door (lower left) and the air gap between the furnace elbow and the dropout chamber (top center). The Sandia sensor location is indicated by the circle.

Sensor data for the furnace off-gas compositions were acquired over a significant portion of the infrared-laser tuning range for more than 60 melts. Several configurations of the data-acquisition equipment were also tested to help determine the susceptibility of the sensor system to various noise sources and to evaluate the possibility of making measurements in a simpler "direct absorption" mode, in contrast to the high-frequency modulation method developed for BOF applications. In addition, concurrent extractive-probe measurements of off-gas composition were made by Stantec Global Technologies, Ltd. The large amount of data (from the TDL sensor, Stantec's extractive probe, and Timken's plant data) taken during more than 60 melts is being analyzed to assess the sensor signal strength throughout the course of a melt and to determine the TDL-wavelength region most likely to be useful for post-combustion control. Observed intensities for CO, CO_2, and H_2O absorption features are being examined for trends during the course of a melt and correlation with process events. Initial examination of the data shows good qualitative agreement between the observed and predicted sensor signals for CO and CO_2 and assures the ability to provide on-line measurement of off-gas temperature.

Results from the on-going data analysis will be used to optimize the design of the prototype for the next phase of the project, long-term plant trials at Timken. These tests are scheduled this summer, 2001.

Sandia National Laboratories
Mail Stop 9056
P.O. Box 969
Livermore, California 94551-0969

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