

Coal Combustion Kinetics Determined for Oxy-Fuel Combustion

Researchers at the CRF have been investigating coal particle combustion characteristics under conditions that simulate burning coal in a mixture of oxygen and re-circulated flue gas. This approach to pulverized coal combustion yields a product of nearly pure carbon dioxide and is being considered as a way to collect and sequester CO_2 to both mitigate against greenhouse gas emissions and enhance domestic recovery of fossil fuels.

Sequestered CO_2 can enhance fossil fuel production if a power plant is situated close to either a suitable coal seam, whereby injecting CO_2 results in coal-bed methane recovery, or to an oil field containing viscous oil, whereby injecting CO_2 results in enhanced oil recovery.

This work is being funded as part of the Department of Energy's National Energy Technology Laboratory (NETL) Advanced Research Program, in collaboration with the Canadian Center for Mineral and Energy Technology (CANMET) in Ottawa, Canada.

The research at the CRF, performed by Chris Shaddix, Jeff Murphy, and Gil Hofacker, has focused on understanding the qualitative impact of enhanced oxygen and CO_2 levels on coal particle combustion and on quantifying the effects of these conditions on coal-char combustion kinetic rates. The kinetic rates generated in this project are being used by CANMET for CFD modeling.

To evaluate the effects of O_2 and CO_2 concentrations on coal particle combustion, samples of coal, approximately 100 micrometers in size, were fed into an upflow, entrained-flow reactor driven by a flat-flame Hencken burner. Pure gases were mixed into the fuel and oxidizer feeds of the burner to yield a constant flame temperature, even as the product gas O_2 concentration was varied from 6-36 mole percent (see Figure 2) and the nitrogen diluent stream was entirely replaced with CO_2 .

A low-sulfur subbituminous coal and a medium-sulfur bituminous coal were characterized. The key diagnostic was a particle-sizing pyrometry system developed at the CRF, which measures the instantaneous temperature and size of individual, burning char particles at a given height in the flow reactor.

A primary question in this work was whether diffusion of oxygen to coal particles limits the char-burning rate under high-oxygen conditions. As expected, the char particles burned at higher temperatures and burned out faster as the oxygen increased from 6-36 mole percent (see Figure 1.)

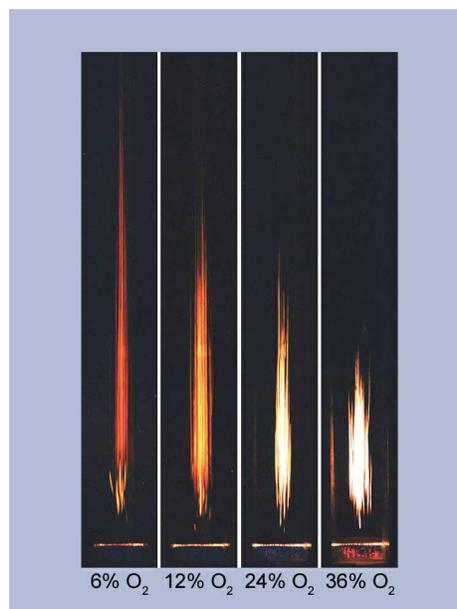


Figure 1. Entrained pulverized coal particles burning in nitrogen environments above the surface of a Hencken burner. The color and lengths of the incandescent particle traces indicate that the char particles burn at a higher temperature and burn out faster as the oxygen concentration increases.

An unexpected result was that enhancing the diffusive driving force at elevated oxygen levels appeared to outweigh the increase in the kinetic burning rate; the char combustion rate was less dominated by diffusion under the high-oxygen conditions. This result shows that, remarkably, it is beneficial to determine char-combustion kinetic rates under elevated oxygen conditions.

Kinetic analysis of the data over the wide range of oxygen levels has shown that the same global kinetic expression may be used to fit all of the data for a given coal, as long as a low value (~ 0.1) is used for the exponent describing the oxygen dependence. This appears to be a consequence of the nearly diffusion-limited burning behavior at low-oxygen levels and the inhibitory effects of ash in the coal char. Further analysis is being conducted to clarify the cause of this result.

Combustion of the coal particles in CO_2 atmospheres resulted in enhanced radiative loss from the hot gases in the entrained-flow reactor and a steeper temperature gradient with height in the reactor. However, after accounting for this effect, for the effect of high CO_2 levels on gas transport properties, and for the effect on gas-to-particle radiative transport, the combustion kinetics of coal char were found to be the same as in N_2 atmospheres.

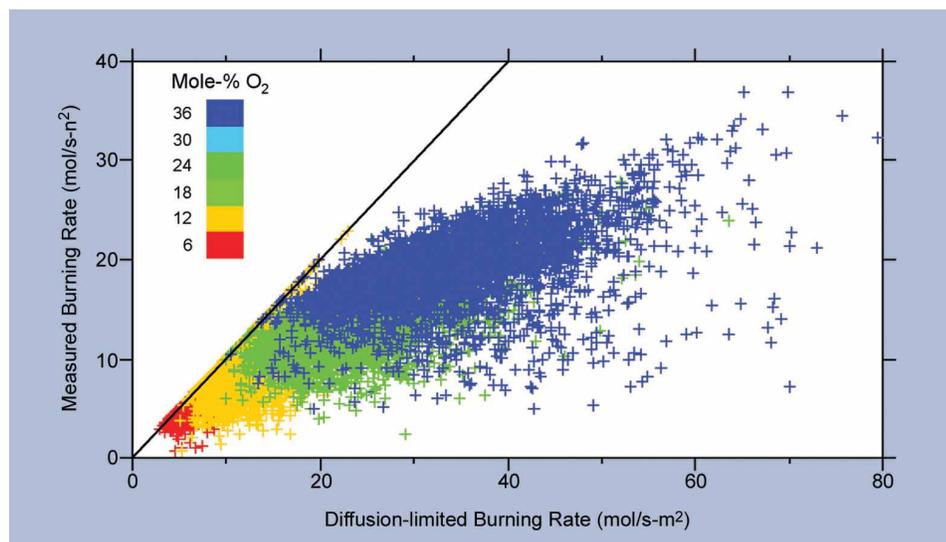


Figure 2. Enhancing the diffusive driving force at elevated oxygen concentrations outweighs the increase in the kinetic burning rate. Researchers found that it is actually beneficial to determine char combustion kinetic rates under elevated oxygen conditions.

Roger Farrow, Tom Settersten, and Paul Schrader have implemented a time-resolved LIF apparatus to investigate collisional quenching of important flame radicals. Through impulsive excitation of radical populations with picosecond lasers and fast fluorescence detection electronics, sub-nanosecond fluorescence decays can be resolved. This capability was demonstrated in initial experiments that yielded room temperature cross sections for the quenching of the $B^1\Sigma^+$ ($v=0$) state of CO (see CRF News Vol. 22, No. 4).

In subsequent experiments, Andreas Dreizler (Technical University of Darmstadt) collaborated with Tom Settersten and Roger Farrow to study the temperature dependence (293-1030 K) of the cross sections for CO quenching. For this work, gas samples were prepared in a temperature- and pressure-controlled fluorescence cell. Seven molecular species were investigated, and the measured quenching rate coefficients are tabulated in Table 1. The thermally averaged quenching cross sections were calculated from the rate coefficients and are plotted as a function (solid curves) of temperature in Figure 1. The cross sections were fit to a power-law dependence on temperature, and the fitting functions agreed to within 5 % of the measured values. Future plans in this area of research include time-resolved CO LIF experiments in low-pressure flames to investigate whether extrapolation of these fitting functions to higher temperatures is valid.

In a recent visit, Jeff Gray (Ohio Northern University) collaborated with Tom Settersten and Brian Patterson to measure species-specific cross sections for collisional quenching of the $A^2\Sigma^+$ ($v=0$) state of NO for temperatures up to 1300 K. This work was motivated by recently reported measurements of the NO $A^2\Sigma^+$ ($v=0$) fluorescence lifetimes in an atmospheric-pressure counter-flow diffusion flame of CH_4 and air (see CRF News Vol. 23, No. 5). In that work, fluorescence lifetimes could not be reconciled with predictions based on accepted quenching cross-section models. In particular, the computed fluorescence lifetimes were substantially lower in the fuel-rich region of the flame for temperatures below 1300 K. In this region of the flame, the dominant quenchers are H_2O and CO_2 , and the accuracy of the quenching models for these species is being investigated in the present study.

Species	Quenching Rate Coefficients ($10^{10} \text{ cm}^3/\text{s}$)			
	293 K	536 K	784 K	1031 K
H_2O	12.9	12.9	13.5	14.0
CO_2	8.25	8.77	9.43	10.3
O_2	5.80	7.39	8.95	10.3
CH_4	7.02	8.34	9.66	10.8
CO	2.45	3.31	4.09	4.69
N_2	1.63	2.46	3.09	3.60
H_2	1.75	3.20	4.49	5.65

Table 1. Rate coefficients for quenching of CO $B^1\Sigma^+$ ($v=0$).

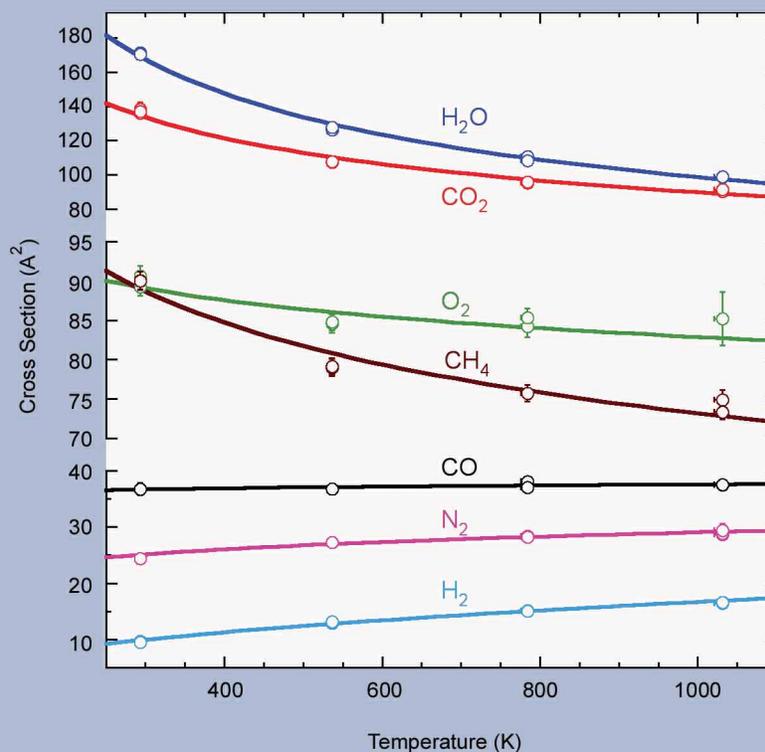
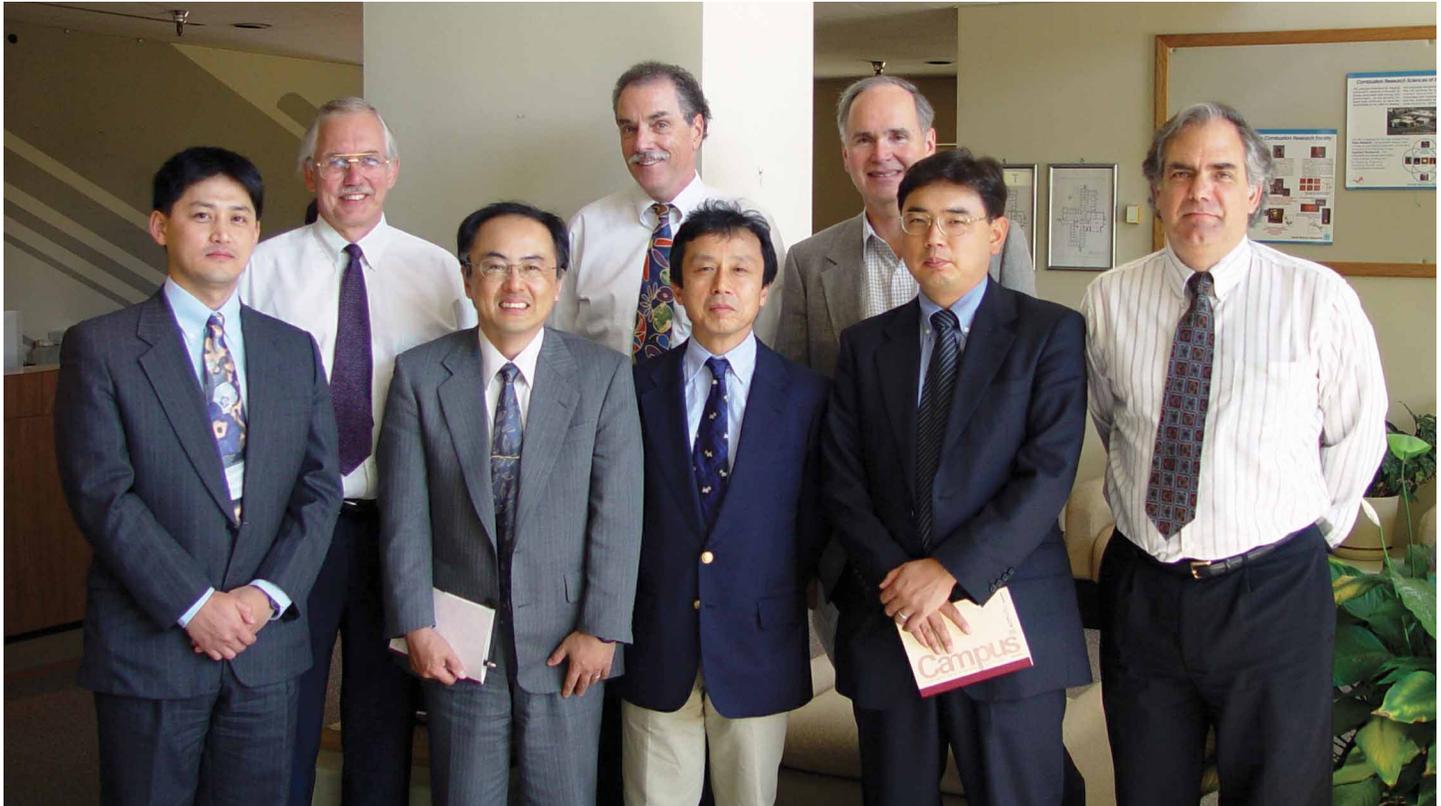


Figure 1. Thermally averaged cross section for collisional quenching of CO $B^1\Sigma^+$ ($v=0$) by H_2 , N_2 , O_2 , CO , H_2O , CO_2 , and CH_4 for temperatures between 293 K and 1030 K. Fitting functions of the form $\sigma(T) = \sigma_0(T/293)^n$ are shown as solid curves.

CRF Hosts Toyota Visit

The CRF recently hosted visitors from Toyota to discuss mutual interests in materials science related to energy production and utilization. In the front row from left to right are Dr. Wen Li (Toyota Technical Center, U.S.), Dr. Hirofumi Shinjoh (Toyota Central Research and Development Labs, Japan), Dr. Shinichi Matsumoto and Mr. Tamara Nakaba, both from Toyota Motor Corporation in Japan, and Jay Keller (Sandia). In the back row (left to right) are Sandians Don Hardesty, Bill McLean, and Dick Steichen, Sandia's Senior Advisor for Industrial Programs.



Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94A185000

Sandia National Laboratories
Mail Stop 9056
P.O. Box 969
Livermore, California 94551-0969
<http://www.ca.sandia.gov/CRF/>

TEMP - RETURN SERVICE REQUESTED



RESORTED
FIRST CLASS
U.S. POSTAGE
PAID
MODESTO, CA
PERMIT NO. 16

Combustion Research Facility NEWS



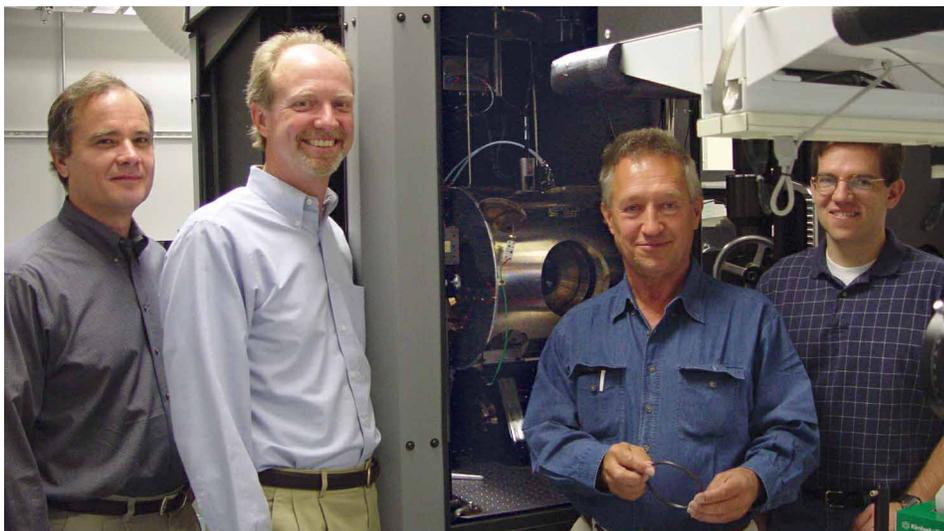
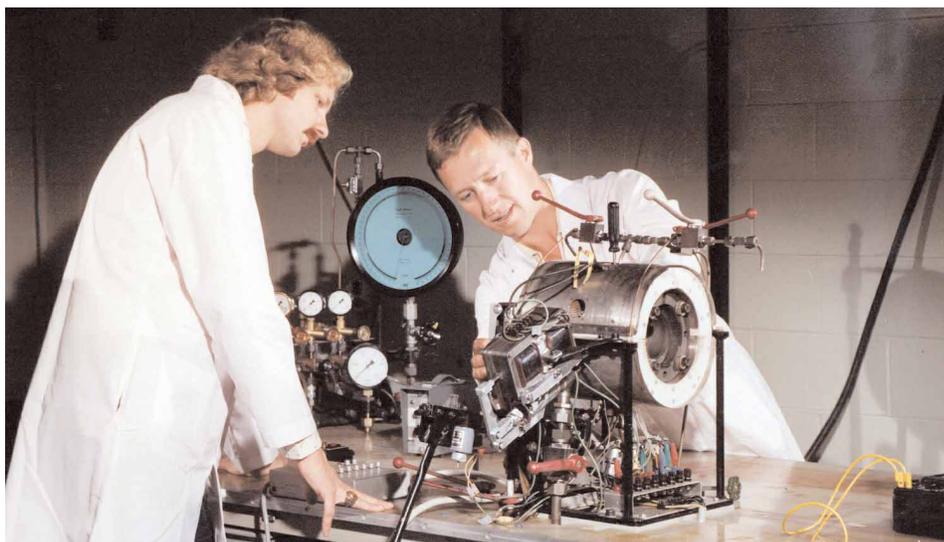
CRF Visitor Recalls the Origins of Combustion Research in Constant-Volume Pressure Vessels

An early and successful avenue of engine research at the CRF has been the study of combustion in constant-volume pressure vessels. Udo Renger's recent visit to the CRF provided an occasion to remember the history of constant-volume reactors and their part in combustion research at the CRF.

Renger, an engineer for Volkswagen Research and Development until his retirement in 1998, returned to the CRF to renew old friendships and see the latest wrinkle in the research he helped start when Volkswagen lent its combustion research vessel to the fledgling CRF.

Renger helped build the constant-volume vessel between 1971 and 1973 for Volkswagen researchers to conduct realistic combustion dynamics experiments. When Dan Hartley, the CRF's first director, saw the research vessel at Volkswagen, he expressed an interest in the work, and Volkswagen offered to lend the vessel to Sandia. After Pete Witze traveled to Germany to see the vessel and advised Hartley to accept Volkswagen's offer, Renger came to Livermore in 1976 to help set it up.

For the next 16 years, Mike Dyer and Dennis Siebers led combustion properties studies using the vessel, modifying and improving it along the way. It also served CRF researchers as a test-bed to develop a suite of laser-based engine diagnostics. Siebers built a completely new vessel in 1992 and the model currently in use in 1995. Recently, researchers have used the vessel to measure the effects of engine parameters on flame lift-off length, which is important in soot formation. Over the years, Sandians have earned several prestigious awards including two SAE awards for research utilizing constant-volume combustion vessels.



Mike Dyer (top left) and Udo Renger (top right) set up the VW constant-volume vessel on its arrival from Germany in 1976. The CRF modifications included diagnostics such as laser shadowgraphs for flow visualization, laser velocimetry for flow velocity and turbulence intensity, and laser refractometry for local flame velocity. Below, three generations of constant-volume researchers stand in front of the latest constant-volume vessel. From left to right are Dennis Siebers, who built the CRF's second- and third-generation vessels, Mike Dyer, who used the VW vessel between 1976 and 1981, Udo Renger, who built the VW vessel, and Lyle Pickett, who is currently conducting research using the CRF's constant-volume vessel.



People People

CRF Appoints New Department Managers

Andy McIlroy and Dennis Siebers were recently named department managers. Andy takes over the Reacting Flow Research Department from Larry Rahn, who was promoted to Senior Scientist in October 2002. Dennis Siebers joins Jay Keller to co-manage the Engine Combustion and Hydrogen Department.

OSA Approves Hope Michelsen as Editor

Hope Michelsen has been selected by the Board of Editors of the Optical Society of America to serve as a Topical Editor for Applied Optics/Lasers, Photonics, & Environmental Optics. Michelsen will be handling manuscripts in the areas of combustion and atmospheric chemical diagnostics and analysis.



Tom Reichardt Works with the National Academy of Sciences on Detection of Chemical Agents

Tom Reichardt has been asked to participate in the National Academy of Sciences Committee on Testing and Evaluation of Standoff Chemical Agent Detectors. The formation of this committee resulted from concerns within the Department of Defense about a previous test and evaluation procedure for instruments designed to detect chemical agents from a remote location. The committee is examining what test protocols should be adopted to ensure that standoff detectors will meet operational requirements and is identifying the challenges associated with the recommended test protocols. A variety of options are being considered, including chamber testing, chamber and simulant testing, and live-agent open-air testing.

Advisory Board Meets at the CRF

The CRF Advisory Board met November 7 and 8, 2002 for their annual review of CRF programs. Participants included Professors Ron Hanson (Stanford), Ed Law (Princeton), Greg McCrae (MIT), Chris Sloane (General Motors), and John Stringer (EPRI).

The CRF News is Published bimonthly by the Combustion Research Facility, Sandia National Laboratories, Livermore, California, 94551-0969.

Director: William J. McLean, Mail Stop 9054

Editors: Jessica Matto, Email: jmatto@sandia.gov

Graphic Artist: Daniel Strong

Laser-Induced Fluorescence Methods Probe HCO Reaction Kinetics

The formyl radical (HCO) is a key radical intermediate in hydrocarbon combustion; because of its role as the principal gateway to CO and CO₂ formation, it is a reliable marker for heat release in flames (see CRF News Vol. 19, No. 4). In work supported by the DOE Office of Basic Energy Sciences, Craig Taatjes, Leonard Jusinski, and John DeSain have recently developed a continuous-wave laser-induced fluorescence (cwLIF) probe to study the kinetics of elementary reactions of the HCO radical. They, along with student intern Andrew Ho, have applied this method to investigations of the rate constant and kinetic isotope effect of the HCO + O₂ reaction.

The cwLIF technique is a powerful method for obtaining extraordinarily precise kinetics measurements. However, its application to HCO was hampered by the difficulty of producing cw radiation at the appropriate wavelength (the B-X system of HCO has its origin near 258 nm). Jusinski determined that Coumarin 521, usually used in pulsed-laser systems, could produce cw 516-nm light with high efficiency and long lifetimes when pumped by the 458-nm line of an Ar⁺ laser. Doubling this light in an external cavity, Jusinski, Taatjes, and DeSain could sensitively measure HCO by cwLIF.

The reaction of HCO with O₂ is one of the most important reactions of HCO in combustion and the only significant removal mechanism for HCO in Earth's atmosphere. The mechanism of the reaction is of fundamental interest as well; the HCO + O₂ reaction is a complex-mediated reaction in which formation of an HCO—O₂ adduct precedes product formation. Rate constants, isotope effects, and branch-

ing fractions in such reactions can display complicated dependences on pressure and temperature. The one previous measurement of the kinetic isotope effect of this reaction indicated a small but significant inverse deuterium kinetic isotope effect; the DCO radical reacted slightly faster than the HCO radical with O₂. An inverse isotope effect can be rationalized if the initially formed HCO—O₂ adduct has a significant probability of dissociating back to reactants rather than proceeding on to products.

However, the reinvestigation of the isotope effect with the cwLIF method

establishes that the reaction has no inverse kinetic isotope effect. The HCO + O₂ and DCO + O₂ rate coefficients are almost identical and are nearly independent of temperature between 296 and 673 K. The temperature dependence of the HCO + O₂ reaction at higher temperatures is significantly smaller than indicated in previous experimental measurements. This difference in temperature dependence may have an important effect on hydrocarbon oxidation models. The observed near-unity deuterium kinetic isotope effect suggests that the initial encounter between HCO and O₂ is rate-limiting, with no significant redissociation of the HCO—O₂ adduct to reactants.

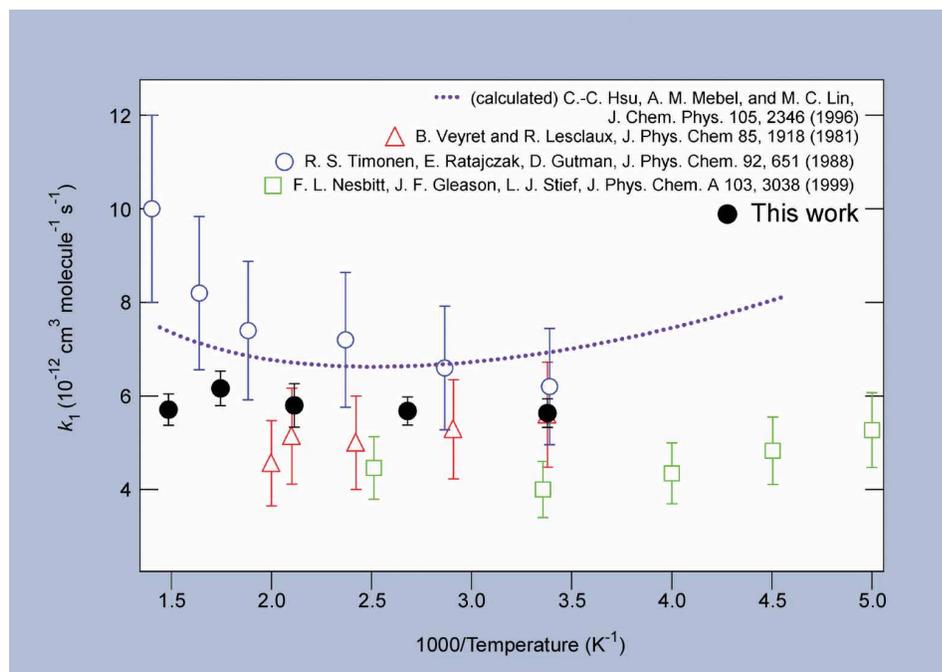


Figure 1. Comparison of the present experimental determination of the HCO+O₂ rate constant to previously published measurements. The temperature dependence of the rate constant differs significantly from previous determinations at the highest temperatures.

Fundamental Data for LIF Quenching Models Obtained by Time-Resolved Picosecond Laser-Induced Fluorescence

Laser-induced fluorescence (LIF) is widely used for sensitive, spatially resolved detection of intermediate species in combustion environments. LIF signals, however, can depend strongly on collisional quenching of the excited-state population, and quantita-

tive determination of species concentrations from LIF measurements requires corrections for variations in the quenching rate. Formulation of a predictive quenching model is possible only if the temperature-dependent, collisional quenching cross-sections for all colli-

sion partners are known. A way to directly and accurately obtain quenching cross sections is to time-resolve the fluorescence signal following short-pulse laser excitation and to then measure the fluorescence decay rate as a function of quencher gas pressure.