**Comprehensive Mechanisms for Combustion Chemistry: An
Experimental and Numerical Study with Emphasis on Applied
Sensitivity Analysis**

Final Report for the Period March 15, 1986 – November 15, 2008
Grant No. DE-FG02—86ER13503

April 2009

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Project Overview

This research project, which extended over seven continuation renewals under the above contract (actually beginning in 1981), addressed fundamental combustion kinetics through an integrated experimental/numerical effort to study the oxidation mechanisms of hydrogen/carbon monoxide/water mixtures and the pyrolysis and oxidation of small oxygenated hydrocarbons under conditions representative of combustion environments.

Over the project duration, fundamental experimental studies were conducted in two large diameter (10 cm) flow reactor facilities, one that operated at reaction temperatures from ~ 1000-~1200 K and at atmospheric pressure, and after 1989, in a second facility that operated at temperatures from 550 K – 1150 K and at pressures from 0.3 atm to 20 atm, with observed reaction times from 10^{-2} to 2 seconds. We conducted gas sampling of stable reactant, intermediate, and product species mole fractions, which provides not only substantial definition of the phenomenology of a pyrolysis/oxidation, but significantly constrains the required behavior that should be exhibited by an appropriate detailed kinetic model under the observed experimental conditions.

In all cases, experiments were performed in such a manner that the chemical species observations are not significantly affected by diffusive coupling. Non-Dispersive Infrared (NDIR), and Fourier Transform Infrared (FTIR) methods were utilized for continuous detection of light hydrocarbons, carbon oxides, oxygenated species, nitrogen oxides and water in a quenched, continuous stream sampled from the flow reactor. More complex mixtures were analyzed off-line using stored gas samples, gas chromatography (GC) and gas chromatography/Fourier Transform Infrared spectrometry (GC/FTIR). Resonance absorption and saturated fluorescence techniques were investigated for determining *in situ* absolute concentrations of OH, NO, CH₃ and some short-lived hydrocarbon species at selected operating conditions for the flow reactor. Radical concentration determinations were not of sufficient accuracy under the dilute, low temperature conditions of flow reactor experiments to significantly improve the modeling constraints of the experimental measurements.

Experimental methodologies for utilizing the flow reactor in studying kinetics included determining the (adiabatic/isothermal) species time-history of a reaction under fixed initial pressure, temperature, and composition; determining the species concentrations present after a fixed reaction time, initial pressure, and composition, for varying initial reaction temperature; studying the pyrolysis of a species in the presence of radical inhibitors; studying the perturbations of a well-defined oxidation reaction system (e.g. CO/H₂/O₂ or H₂/O₂), operated under one of the above modes, by the seeding the reaction with small amounts of an additional species.

In research after 1995, an atmospheric-pressure, premixed laminar wall stagnation flame burner facility was added to expand experimental investigations to include laminar burning rate properties at atmospheric pressure. As our experience grew, we transitioned the experimental efforts at Princeton by moving to experimental collaborations with Dr. Yiguang Ju, who has

invested heavily in both opposed jet stagnation and high pressure bomb approaches to studying laminar burning rate properties.

Over the entire project, collaborations with other investigators that were developing applied mathematical analysis tools, or performing laminar flame, shock tube or rapid compression machine kinetic studies have been key to developing the comprehensive kinetic models produced through this research. Our project has also contributed to elementary kinetic rate determinations for several key reactions, notably $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$, $\text{CH}_3 + \text{HO}_2 = \text{CH}_3\text{O} + \text{OH}$, $\text{H}_2 + \text{NO}_2 = \text{HONO} + \text{H}$, $\text{SO}_2 + \text{O} (+\text{M}) = \text{SO}_3 (+\text{M})$, and the ethanol decomposition reactions, particularly $\text{C}_2\text{H}_5\text{OH} = \text{C}_2\text{H}_4 + \text{H}_2\text{O}$, which are key reactions in high pressure energy conversion systems. In addition, modeling of the species histories that we have obtained have pointed to the need to consider elementary reaction rate uncertainties of other reactions.

Of particular mention are the following collaborations: elementary kinetic rate constant studies with Dr. Joe Michael at Argonne National laboratories; Dr. Phillip Westmoreland's research on low pressure molecular beam studies of laminar premixed flames; more recent collaborations with research teams pursuing low pressure laminar premixed flame molecular beam studies at the ALS facility at Lawrence Berkeley Laboratories, particularly Drs. Terry Cool and Nils Hansen; and Dr. Yiguang Ju at Princeton University in syngas laminar flame studies at high pressure. We have also investigated two stage ignition phenomena within this project for dimethyl ether, methyl formate, acetaldehyde, ethanol, and n-heptane. Collaborations with the rapid compression machine studies of Dr. C-J (Jackie) Sung at Case Western Reserve University have significantly added to the success of these pursuits. Collaborations with Dr. H.C. Curran on research involving dimethyl ether and methyl formate have also been contributory in evolving reaction models for these species.

Numerical studies have been key to progress made throughout this project, as they have been utilized to guide selection of experimental conditions that constrain modeling parameters; to interpret observations that would permit determination of specific rate constant information; for developing, refining and/or extending the predictive range of mechanism constructs using the new experimental data and literature results; and to study the effects of diffusive transport coupling on reaction behavior in premixed and diffusion flames. Hierarchical, comprehensive model development methods, initially conceived through collaborations with Dr. C.K. Westbrook of Lawrence Livermore Laboratories in the early 1980's, have been applied to develop and refine detailed kinetic mechanisms that best predict experimental measurements.

In several cases, new applied mathematical methods of analyses have emerged as part of these studies, especially based upon the early efforts of Dr. Richard Yetter, and Dr. Hershel Rabitz at Princeton on gradient elementary and feature sensitivity analyses, and more recently, through contributions from Dr. Andre Kazakov and Dr. Marcos Chaos as Professional Research Staff in our/this/my? group in applying computational singular perturbation approaches.

The principal methodologies that have been applied throughout this project are related to three approaches: (1) utilizing the perturbations of the H_2/O_2 and $\text{CO}/\text{H}_2\text{O}$ /oxidant reaction systems by the addition of small amounts of other species to further clarify elementary reaction properties; (2) utilizing radical inhibitors in pyrolysis studies to obtain measurements of the initial species decomposition; (3) further elucidating the reaction mechanisms for the pyrolysis and oxidation

of small oxygenates (aldehydes, alcohols, and especially ethers) and olefinic species through flow reactor/laminar flame measurements, and numerical modeling.

In 2006, I seriously considered reducing my research involvement and concentrating on other academic endeavors, and so, after twenty-two years, I procrastinated in submitting another renewal proposal. This decision was not made based upon professional issues or lack of new ideas and directions, but on personal circumstances. From late 2007 to present, my views have changed considerably, and recently, I have joined a number of colleagues in writing a submittal to the Energy Frontiers Research Center Initiative, now in evaluation. If we are successful in establishing this center, I will be continuing my interests in oxygenated hydrocarbon combustion kinetics within this program, but otherwise, I will further contemplate re-establishing a single investigator project in this area. Much remains in terms of results from the present project that needs to be brought to the archival literature, and I will continue to do this through collaborations with prior staff and collaborators that have been involved previously. Below, we briefly summarize the archivally published papers already in the literature as a result of this project, each giving the details of the research. This is followed by a summary presentation of ongoing efforts that have resulted in preprinted literature and which we are concentrating on bringing to the archival literature at this time. We will continue to populate our laboratory website over the near term with the reaction models associated with both archival and pre-printed literature, inclusive of updates that may come forth.

Summary of Research Conducted under During this Project

The research conducted in this project has produced a large number of archival and pre-preprints on hydrogen-oxygen/carbon monoxide reaction systems, and oxygenated hydrocarbon pyrolysis and oxidation kinetics. The archival works provide detailed descriptions of the associated research that have received peer review. Appendix A of this final report chronologically lists these archival publications, and the details of each paper will not be discussed further here. It should be mentioned, however, that there are some key papers that describe the experimental and numerical methodologies used in our program to interpret experimental data from flow reactors and to compare plug flow computations with flow reactor experimental results. The key flow reactor experimental papers are denoted with a single asterisk (*), while those of most impact in how numerical computations should be compared with flow reactor results and denoted with a double plus (++).

Recent Progress

This project also resulted in a large number of preprint papers and presentations. Appendix B lists the preprinted works associated with the overall project from 2003 to present, as several of these works are continuing. Those that we expect to bring to archival publication in the future are are marked with a “C”.

Graduate Theses Completed under this Project

1	"Experimental and Numerical Studies of Ethanol Chemical Kinetics", Juan Li, Ph.D. Thesis, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, June 2004. MAE 3122-T.
2	"Laminar Flame Speed Study using Particle Image Velocimetry on a Stagnation Flame Configuration", Zhenwei Zhao, M.S.E. Thesis, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, December 2002. MAE 3096-T.
3	"Determination of Elementary Rate Constants by Fitting Complex Reaction Mechanisms: Application to Intermediate-Temperature Hydrocarbon Kinetics", J. J. Scire Jr., Ph.D. Thesis, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, June 2002. MAE 3101-T.
4	"The Oxidation of Carbon Monoxide/Hydrogen/Oxygen/NO _x /SO _x Mixtures in a High Pressure Flow Reactor", Mark A. Mueller, Ph.D. Thesis, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, June 2000. MAE 3066-T.
5	"Chemical Kinetics of Di-methyl Ether, a Turbulent Flow Reactor Study" Susan Fischer, M.S.E. Thesis, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, January, 1999. MAE 3035-T.
6	"Study of Acetaldehyde Combustion Kinetics in a Variable Pressure Flow Reactor", Darcy C.Z. Zarubiak, M.S.E. Thesis, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, June 1997. MAE 2044-T.
7	"An Experimental Study of Supersonic Laminar Reacting Boundary Layers", Joseph Fielding, M.S.E. Thesis, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, January 1997. MAE 2090-T.
8	"Sensitization of the CO/H ₂ /O ₂ System by Hydrocarbon Addition", T. Kim, M.S.E. Thesis, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, January, 1994, MAE 1987-T.
9	"The Oxidation of Methanol, Isobutene, and Methyl tertiary-Butyl Ether", T. Held, Ph.D. Thesis, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, August, 1993, MAE 1978-T.
10	"A Variable Pressure Flow Reactor for Chemical Kinetic Studies: Hydrogen, Methane, and Butane Oxidation at 1 to 10 Atmospheres and 880 to 1040 K", M.L. Vermeersch, Ph.D. Thesis, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, August, 1991, MAE 1916-T.
11	"An Experimental and Numerical Study on the Oxidation of Formaldehyde" S. Hochgreb, Ph.D. Thesis, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, April, 1991, MAE 1910-T.
12	"Trace Radical Species Detection in a Turbulent Chemical Kinetic Flow Reactor Using a 180° Laser Induced Fluorescence Probe", G.T. Linteris, Ph.D. Thesis (Prof. I. Glassman, co-advisor), Department of Mechanical and Aerospace Engineering, Princeton University, Princeton NJ, January, 1990, MAE 1880-T.
13	"The Combustion Chemistry of Simple Alcohol Fuels", T.S. Norton, Ph.D. Thesis, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton NJ, January 1990, MAE 1877-T.

14	"An Experimental/Numerical Study of Carbon Monoxide-Hydrogen-Oxygen Kinetics with Applications of Gradient Sensitivity Analysis", R.A. Yetter, Ph.D. Thesis, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, June 1985, MAE 1730-T.
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Attached Manuscripts

Manuscripts of papers that are to appear in press and those that are in preparation for archival publications (presently preprints) are attached to this summary.

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Appendix A – Archival Publications of Research Funded in whole or part by this Project

1	(with M. Chaos, M. P. Burke, and Y. Ju), “Syngas Chemical Kinetics and Reaction Mechanisms”, Chapter 2 in <i>Syngas Combustion</i> , (Editors: Tim C. Lieuwen, Vigor Yang, Richard A. Yetter), Elsevier, (2009). In Press.
2	(with M. P. Burke, Z. Chen, and Y. Ju), “Effect of Cylindrical Confinement on the Determination of Laminar Flame Speeds Using Outwardly Propagating Flames”, <i>Combust. Flame</i> (2009). DOI:10.1016/j.combustflame.2009.01.013
3	(with J. Wang, M. Chaos, B. Yang, T. A. Cool, T. Kasper, N. Hansen, P. Oßwald, K. Kohse-Höinghaus and P. R. Westmoreland), “Composition of Reaction Intermediates for Stoichiometric and Fuel-rich Dimethyl Ether Flames: Flame Sampling Mass Spectrometry and Modeling Studies”, <i>Phys. Chem. Chem. Phys.</i> (2009). DOI: 10.1039/b815988b
4	(with C.K. Westbrook, W.J. Pitz, P.R. Westmoreland, M. Chaos, Oßwald, K. Kohse-Höinghaus, T.A. Cool, J. Wang, B. Yang, N. Hansen, T. Kasper), “A Detailed Chemical Kinetic Reaction Mechanism for Oxidation of Four Small Alkyl Esters in Laminar Premixed Flames,” <i>Proc. Combust. Ins.</i> 32, 221-228 (2009).
5	(with G. Mittal, M. Chaos, C-J. Sung), “Dimethyl Ether Autoignition in a Rapid Compression Machine: Experiments and Chemical Kinetic Modeling”, <i>Fuel Proc. Tech.</i> 89, 1244-1254 (2008).
6	(with M. Chaos), “Syngas Combustion Kinetics and Applications”, in Special Issue: <i>Syngas Combustion</i> (V. Yang and T. Lieuwen, eds.) <i>Combustion Sci. Tech.</i> 180, 1051-1094 (2008).
7 ++	(with Z. Zhao, M. Chaos, and A. Kazakov), “Thermal Decomposition Reaction and a Comprehensive Kinetic Model of Dimethyl Ether”, <i>Int J. Chem. Kin.</i> 40, 1-18 (2008).
8	(with M. Chaos), “Ignition of Syngas/air and Hydrogen/air Mixtures at Low Temperatures and High Pressures: Experimental Data Interpretation and Kinetic Modeling Implications, <i>Combust. Flame</i> 152, 293-299 (2008).
9	(with J. Li, Z. Zhao, A. Kazakov, and M. Chaos), “A Comprehensive Kinetic Mechanism for CO, CH ₂ O, CH ₃ OH Combustion”, <i>Int. J. Chem. Kin.</i> 39, 109-136 (2007).
10	(with M. Chaos), “Ignition of Syngas/air and Hydrogen/air Mixtures at Low Temperatures and High Pressures: Experimental Data interpretation and Kinetic Modeling Implications, <i>Combust. Flame</i> 152, 293-299 (2008).
11	(with J. Li, Z. Zhao, A. Kazakov, and M. Chaos), “A Comprehensive Kinetic Mechanism for CO, CH ₂ O, CH ₃ OH Combustion”, <i>Int. J. Chem. Kin.</i> 39, 109-136 (2007).
12	(with S. Gaïl, M. Thomson, S. M. Sarathy, S. A. Syed, P. Dagaut, Pascal Diévar, and A. J. Marchese), “A Wide Range Kinetic Modeling Study of Methyl Butanoate Combustion”, <i>Proc. Comb. Ins.</i> 31, 305-311 (2007).
13	(with Z. Chen, X. Qin, Y. Ju, Z. Zhao, and M. Chaos), “High Temperature Ignition and Combustion Enhancement by Dimethyl Ether Addition to Methane-Air Flames”, <i>Proc. Comb. Ins.</i> 31, 1215-1222 (2007).

14	(with T. A. Cool, J. Wang, N. Hansen, P. R. Westmoreland, Z. Zhao, A. Kazakov, T. Kasper, and K. Kohse-Höinghaus), “Chemistry of Fuel-rich Dimethyl Ether Flames Using Combined Photoionization Molecular-Beam Mass Spectrometry and Modeling” <i>Proc. Comb. Ins.</i> 31, 285-293 (2007).
15	(with W. J. Pitz, N. P. Cernansky, F. N. Egolfopoulos, J.T. Farrell, D. G. Friend, H. Pitsch), “Development of an Experimental Database and Chemical Kinetic Models for Surrogate Gasoline Fuels”, SAE paper 2007-01-0175 (2007). Published in SAE Proceedings 2007.
16 ++	(with M. Chaos, A. Kazakov, and Z. Zhao), “Computational Singular Perturbation Analysis of Two Stage Ignition of Large Hydrocarbons”, <i>J. Phys. Chem A.</i> 110, 7003-7009 (2005).
17 ++	(with Z. Zhao, J. Li, and A. Kazakov), “Temperature-Dependent Feature Sensitivity Analysis for Combustion Modeling”, <i>Int. J. Chem. Kin.</i> 37: 282-295 (2005).
18 *	(with J. Li, and A. Kazakov), “Experimental And Numerical Studies of Ethanol Decomposition Reactions”, <i>J. Phys. Chem. A</i> 108, 7671-7680 (2004).
19	(with Z. Zhao, and A. Kazakov), “Measurements of DME/Air Mixture Burning Velocities by Using Particle Image Velocimetry”, <i>Combust. Flame</i> 139, 52-60 (2004).
20	(with J. Li, Z. Zhao, and A. Kazakov), “An Updated Comprehensive Kinetics Model of H ₂ Combustion”, <i>Int. J. Chem. Kin.</i> 36, 566 (2004).
21	(with Z. Zhao, A. Kazakov, and J. Li), “The Initial Temperature And N ₂ Dilution Effect On The Laminar Flame Speed Of Propane/Air Mixtures”, <i>Combust. Sci. Tech.</i> 176, 1705 (2004).
22	(with T. Carriere, P.R. Westmoreland, A. Kazakov, and Y.S. Stein), “Modeling Ethylene Combustion From Low To High Pressure”, <i>Proc. Comb. Ins.</i> 29, 1257-1266 (2002).
23 ++	(with J.J. Scire and R.A. Yetter), “Comparison of Global and Local Sensitivity Techniques for Rate Constants Determined using Complex Reaction Mechanisms”, <i>Int. J. Chem. Kin.</i> 33, 780 (2001).
24	(with J. Li and A. Kazakov), “Ethanol Pyrolysis Experiments in a Variable Pressure Flow Reactor”, <i>Int. J. Chem. Kin.</i> 33, 859 (2001).
25 ++ *	(with J. J. Scire, Jr. and , S. D. Klotz), "Initial Observations of Ketene in Flow Reactor Kinetic Studies", <i>Zeitscheift fur Physikalishche Chemie</i> 215, 1011-1023 (2001).
26 *	(with J. J. Scire, Jr. and R. A. Yetter), "Flow Reactor Studies of Methyl Radical Oxidation Reactions in Methane Perturbed Moist Carbon Monoxide Oxidation at High Pressure with Model Sensitivity Analysis", <i>Int. J. Chem. Kin.</i> 39, 75 (2001).
27	(with S.P. Zeppieri and S.D. Klotz), “Modeling Concepts for Larger Carbon Number Alkanes: A Partially Reduced Skeletal Mechanism for n-Decane Oxidation and Pyrolysis”, <i>Proc. Combust. Ins.</i> 28, 1587 (2000).
28 ++	(with J.C. Lee, R.A. Yetter, A.G. Tomboulides, and S.A. Orszag), “Simulation and Analysis of Laminar Flow Reactors”, <i>Combust. Sci. Tech.</i> 159, 199 (2001).
29	(with S.L. Fischer and H.J. Curran), “The Reaction Kinetics of Di-Methyl Ether. I: High Temperature Pyrolysis and Oxidation in Flow Reactors”, <i>Int. J. Chem. Kin.</i> 32, 713 (2000).

30	(with S.L. Fischer and H.J. Curran), "The Reaction Kinetics of Di-Methyl Ether. II: Low Temperature Oxidation in Flow Reactors", <i>Int. J. Chem. Kin.</i> 32, 741 (2000).
31	(with M.A. Mueller and R.A. Yetter), Kinetic Modeling of the CO/H ₂ O/O ₂ /NO/SO ₂ System: Implications for High-Pressure Fall-off in the SO ₂ +O(+M) = SO ₃ (+M) Reaction, <i>Int. J. Chem. Kin.</i> 32, 317 (2000).
32 *	(with M.A. Mueller, J.L. Gatto, T.J. Kim, and R.A. Yetter), "Hydrogen/Nitrogen Dioxide Kinetics: Derived Rate Data for the Reaction H ₂ +NO ₂ = HONO+H at 833 K, <i>Combust. Flame</i> 120, 589 (1999).
33	(with M.A. Mueller, T.J. Kim, and R.A. Yetter), "Flow Reactor and Kinetic Modeling Studies of the H ₂ /O ₂ /NO _x and CO/H ₂ O/O ₂ /NO _x Reactions", <i>Int. J. Chem. Kin.</i> 31, 705 (1999).
34	(with M.A. Mueller, T.J. Kim, and R.A. Yetter), "Flow Reactor and Kinetic Modeling Studies of the H ₂ /O ₂ Reaction", <i>Int. J. Chem. Kin.</i> 31, 113 (1999).
34	(with T. Amano), "Effect of Dimethyl Ether, NO _x , and Ethane on CH ₄ Oxidation; High Pressure, Intermediate Temperature Experiments and Modeling", <i>27th Symposium (Intn'l) on Combustion</i> , The Combustion Institute, Pittsburgh, PA., 1998. pp. 397.
36	(with H.J. Curran, W.J. Pitz, C.K. Westbrook, and C.V. Callahan) "Oxidation of Automotive Primary Reference Fuels in a High Pressure Flow Reactor", <i>27th Symposium (Intn'l) on Combustion</i> , The Combustion Institute, Pittsburgh, PA., 1998. pp. 379.
37 *	(with M. A. Mueller and R.A. Yetter), "Measurement of the Rate Constant of H+O ₂ +M=HO ₂ +M (M=N ₂ , Ar) Using Kinetic Modeling of the High Pressure H ₂ /O ₂ /NO _x Reaction", <i>27th Symposium (Intn'l) on Combustion</i> , The Combustion Institute, Pittsburgh, PA., 1998. pp. 177.
38 *	(with T.J. Held), "A Comprehensive Mechanism for Methanol Oxidation", <i>Int. J. Chem. Kin.</i> 30, 805 (1998).
39	(with T.J. Held and A.J. Marchese), "A Semi-Empirical Reaction Mechanism for N-Heptane Oxidation and Pyrolysis", <i>Combust. Sci. Tech.</i> 123, 107 (1997).
40 *	(with T.J. Held), "An Experimental and Computational Study of Methanol Oxidation in the Intermediate and High Temperature Regimes", <i>25th Symposium (Int'l) on Combustion</i> , The Combustion Institute, Pittsburgh, PA., 1994. p. 901.
41	(with T.J. Kim and R.A. Yetter), "New Results on Moist CO Oxidation: High Pressure, High Temperature Experiments and Comprehensive Kinetic Modeling", <i>25th Symposium (Int'l) on Combustion</i> , The Combustion Institute, Pittsburgh, PA., 1994. p.759.
42	(with C. Corre, W.J. Pitz, and C.K. Westbrook), "Two-Stage n-Butane Flame: A Comparison Between Experimental Measurements and Modeling Results", <i>24th Symposium (Int'l) on Combustion</i> , The Combustion Institute, Pittsburgh, PA, 1992. p. 843.
43	(with R.A. Yetter), "Inhibition of Moist Carbon Monoxide Oxidation by Trace Amounts of Hydrocarbons", <i>24th Symposium (Int'l) on Combustion</i> , The Combustion Institute, Pittsburgh, PA, 1992. p. 757.
44	(with S. Hochgreb), "A Comprehensive Study on CH ₂ O Oxidation Kinetics", <i>Combust. Flame</i> 91, 257 (1992).
45	(with S. Hochgreb), "Decomposition of 1,3,5-Trioxane at 700-800 K", <i>J. Phys. Chem.</i> 96, 295 (1992).

46	(with T.S. Norton), "An Experimental and Modeling Study of Ethanol Oxidation Kinetics in an Atmospheric Pressure Flow Reactor", <i>Int. J. Chem. Kin.</i> 24, 319 (1992).
47	(with R.A. Yetter and D.M. Golden), "Combustion Kinetics for High Speed Chemically Reacting Flows", An invited Contribution to <u>Major Research Topics in Combustion</u> , ICASE/NASA Series, M.Y. Hussaini, A. Kumar and R.G. Voigt, eds., Springer-Verlag, NY, 1992. p. 309.
48	(with G.T. Linteris, R.A. Yetter, and K. Brezinsky), "Hydroxyl Radical Concentration Measurements in Moist Carbon Monoxide Oxidation in a Chemical Kinetic Flow Reactor", <i>Combust. Flame</i> 86, 162 (1991).
49	(with R.A. Yetter, and H. Rabitz), "A Comprehensive Reaction Mechanism for Carbon Monoxide/Hydrogen/Oxygen Kinetics", <i>Combust. Sci. Tech.</i> 79, 97 (1991).
50	(with R.A. Yetter, and H. Rabitz), "Flow Reaction Studies of Carbon Monoxide/Hydrogen/Oxygen Kinetics", <i>Combust. Sci. Tech.</i> 79, 129 (1991).
51	(with R.A. Yetter, H. Rabitz, R.C. Brown, and C.E. Kolb), "Kinetics of High Temperature B/O/H/C Chemistry", <i>Combust. Flame</i> 83, 43 (1991).
52	"The Phenomenology of Modeling Combustion Chemistry", Part 1, Chapter 3, <u>Fossil Fuel Combustion - A Sourcebook</u> , W. Bartok and A.F. Sarofim, eds., John Wiley and Sons Inc., NY. 1991.
53	(with S. Hochgreb, and R.A. Yetter), "The Oxidation of CH ₂ O in the Intermediate Temperature Range (943-995 K)", <i>23rd Symposium (Int'l) on Combustion</i> , The Combustion Institute, Pittsburgh, PA 1990. p. 171.
54	(with T.S. Norton), "The Flow Reactor Oxidation of C ₁ - C ₄ Alcohols and MTBE", <i>23rd Symposium (Int'l) on Combustion</i> , The Combustion Institute, Pittsburgh, PA, 1990. p. 179.
55	(with G.T. Linteris and K. Brezinsky), "A High Temperature 180 Degree Laser Induced Fluorescence Probe for Remote Trace Radical Concentration Measurements, <i>Applied Optics</i> 30, 381 (1990).
56	(with T.S. Norton), "Toward a Comprehensive Mechanism for Methanol Pyrolysis", <i>Int. J. Chem. Kin.</i> 22, 219 (1990).
57	(with R.A. Yetter, H. Rabitz, R.B. Klemm, and R.G. Maki), "Evaluation of the Rate Constant for Reaction OH+H ₂ CO: Application of Modeling and Sensitivity Analysis Techniques for Determination of the Product Branching Ratio", <i>J. Chem. Phys.</i> 91, 4088 (1989).
58	(with T.S. Norton), "Some New Observations on Methanol Oxidation Chemistry", <i>Combust. Sci. Tech.</i> 63, 107 (1989).
59	(with M.D. Smooke, H. Rabitz, and Y. Reuven), "Application of Sensitivity Analysis to Pre-mixed Hydrogen-Air Flames", <i>Combust. Sci. Tech.</i> 59, 295 (1988).
60	(with R.A. Yetter and H. Rabitz), "Complications of One-Step Kinetics For Moist CO Oxidation", <i>21st Symposium (Int'l) on Combustion</i> , The Combustion Institute, Pittsburgh, PA., 1987, p. 749.
61	(with E.I. Axelsson, K. Brezinsky, W.J. Pitz, and C.K. Westbrook), "Chemical Kinetic Modeling of the Oxidation of Large Alkane Fuels : N-Octane and Iso- Octane", <i>21st Symposium (Int'l) on Combustion</i> , Pittsburgh, PA., 1987, p. 783.

62	(with K. Brezinsky), "A Flow Reactor Study of the Oxidation of n-Octane and Iso-Octane", <i>Combust. Sci. Tech.</i> 47, 199 (1986).
63	(with K. Brezinsky), "A Flow Reactor Study of the Oxidation of Iso-butylene and an Iso-butylene /n-octane Mixture", <i>Combust. Sci. and Tech.</i> 47, 225 (1986).
64 ++	(with R.A. Yetter and H. Rabitz), "Some Interpretive Aspects of Elementary Sensitivity Gradients in Combustion Kinetics Modeling", <i>Combust. Flame</i> 59, 107 (1985).
65 ++	(with R.A. Yetter, L.A. Eslava and H. Rabitz), "Elementary and Derived Sensitivity Information in Chemical Kinetics", <i>J. Phys. Chem.</i> 88, 1497 (1984).
66	(with C.K. Westbrook and K.P. Schug), "Numerical Modeling of Ethylene Oxidation in Laminar Flames", <i>Combust. Flame</i> 52, 299 (1983).
67	(with C.K. Westbrook and K.P. Schug), "A Comprehensive Mechanism for the Pyrolysis and Oxidation of Ethylene", <i>19th Symposium (Int'l) on Combustion</i> , The Combustion Institute, Pittsburgh, PA, 1983, p. 153.
68 ++	(with C.K. Westbrook), "Simplified Reaction Mechanisms for the Oxidation of Hydrocarbon Fuels in Flames", <i>Combust. Sci. Tech.</i> 27, 31 (1981).

**Appendix B-Preprints/Presentations of Research 2004-Present in
Preparation for Future Publication (2003 – 2008)**

1 C	(with S. Dooley, M.P. Burke, M. Chaos, Y. Stein, F.L. Dryer, V.P. Zhukov, O. Finch, C.A. Daly, J.M. Simmie, H.J. Curran), <i>Methyl Formate Oxidation</i> , 2009. (Archival Manuscript in Preparation)
2	(with S. Dooley, M.P. Burke, M. Chaos, Y. Stein, V.P. Zhukov, O. Finch, C.A. Daly, J.M. Simmie, H.J. Curran), <i>An Experimental and Kinetic Modeling Study of Methyl Formate Oxidation</i> , 5 th European Combustion Meeting 2009, Vienna University of Technology, Austria
3	(with S. Dooley, M. Chaos, H.J. Curran, B. Yang, J. Wang, T. A. Cool, T. Kasper, N. Hansen), <i>An Experimental and Kinetic Modeling Study of Methyl Formate Low-Pressure Flames</i> , 6 th U.S. National Combustion Meeting 2009, Ann Arbor, Michigan.
4 C	(with M. Chaos), “Chemical-Kinetic Modeling of Ignition Delays: Considerations in Interpreting Shock Tube Data”, Int. J. Chemical Kinet. (Submitted) July 2008.
5	(with M.P. Burke, M. Chaos, and Y. Ju), “Pressure Dependence of H ₂ and H ₂ /CO Laminar Flame Speeds”, 32 nd International Symposium on Combustion, McGill University, Canada, August 3-8, 2008. Work in Progress Poster W4P 181
6	(with F.M. Haas, and M. Chaos), “Low and Intermediate Temperature Oxidation Kinetics of PRF-Ethanol Blends”, 32 nd International Symposium on Combustion, McGill University, Canada, August 3-8, 2008. Work in Progress Poster W5P 083
7	(with P. R. Westmoreland, T. A. Cool, N. Hansen, T. Kasper, K. Kohse-Höinghaus, M. E. Law, W. Li, P. Oßwald, U. Struckmeier, C. K. Westbrook, B. Yang, J. Wang), “Recent Results of MBMS for Flame Characterization and Kinetics”, 2008 Technical Meeting, Central States Section of the Combustion Institute, Bryant Conference Center, University of Alabama, April 20-22, 2008. Invited Presentation by P.R. Westmoreland.
8	(with M. Colket, T. Edwards, S. Williams, N. P. Cernansky, D. L. Miller, F. Egolfopoulos, J. Bellan, P. Lindstedt, K. Seshadri, H. Pitsch, A. Sarofim, M. Smooke, and W. Tsang), Identification of Target Validation Data for Development of Surrogate Jet Fuels, 2008 Aerospace Sciences Meeting American Institute of Aeronautics and Astronautics, Reno, Nevada, January 6-10, 2008. AIAA2008-972
9	(with M. P. Burke, and Y. Ju), “Effect of Flow Field Perturbations on Laminar Flame Speed Determination Using Spherical Flames”, 2008 Aerospace Sciences Meeting American Institute of Aeronautics and Astronautics, Reno, Nevada, January 6-10, 2008.
10	(with M.P. Burke and Y. Ju), “Effect of Cylindrical Confinement on the Evolution of Outwardly Propagating Flames”, 2007 Fall Eastern States Section Meeting of the Combustion Institute, University of Virginia, Oct. 21-24.
11	(with G. Mittal, M. Chaos, and S-J Sung), “A Rapid Compression Machine Study of Dimethyl Ether Autoignition”, 2007 Fall Eastern States Section Meeting of the Combustion Institute, University of Virginia, Oct. 21-24.

12	(with M.P. Burke, X. Qin, and Y. Ju), “Measurements of Hydrogen Syngas Flame Speeds at Elevated Pressures”, 5 th US Combustion Meeting, University of California at San Diego, San Diego, CA, March 25-28, 2007. Paper A-16.
13 C	(with J. Li, A. Kazakov, and M. Chaos), “Chemical Kinetics of Ethanol Oxidation”, 5 th US Combustion Meeting, University of California at San Diego, San Diego, CA, March 25-28, 2007. Paper C-26.
14	(with J.T. Farrell, N.P. Cernansky, F.L. Dryer, D.G. Friend, C.A. Hergart, C. K. Law, R.M. McDavid, C.J. Mueller, A.K. Patel, and H. Pitsch), “Development of an Experimental Database and Kinetic Models for Surrogate Diesel Fuels”, SAE paper 07PFL-676 (2007) SAE World Congress & Exhibition, April 16, 2007.
15	(with W. J. Pitz, N. P. Cernansky, F. N. Egolfopoulos, J.T. Farrell, D. G. Friend, H. Pitsch), “Development of an Experimental Database and Chemical Kinetic Models for Surrogate Gasoline Fuels”, SAE paper 2007-01-0175 (2007) SAE World Congress & Exhibition, April 16, 2007.
16	(with M. Colket, N.P. Cernansky, C. K. Law, F. Egolfopoulos, D. Friend, D. B. Lenhert, P. Lindstedt, H. Pitsch, A. Sarofim, K. Seshadri, M. Smooke, W. Tsang, S. Williams and T. Edwards), “Development of an Experimental Database and Kinetic Models for Surrogate Jet Fuels”, AIAA Annual Conference, Reno NV, January, 2007. Paper No. AIAA-2007-770
17	(with M. Chaos, Z. Zhao, and A. Kazakov), “An Experimental and Kinetic Study of Acetone Oxidation in a Flow Reactor”, Work in Progress Poster, 31 st International Symposium on Combustion, University of Heidelberg, Germany, August 6-11 2006. Available at: http://www.princeton.edu/~combust/
18	(with A. Kazakov, M. Chaos, and Z. Zhao), “Computational Singular Perturbation Analysis of <i>n</i> -Heptane Two-Stage Ignition”, Eastern States Section Fall Meeting, the Combustion Institute, Orlando, FL November 14,15, 2005. Extended Abstract
19	(with A. Kazakov, Z. Zhao, and B. D. Urban), “Do We Understand How Two-stage Hydrocarbon Ignition Mechanisms Work?”, 6 th International Conference on Chemical Kinetics, Holiday Inn, Gaithersburg, MD. July 25-29, 2005. Poster L15
20	(with J. Li and A. Kazakov), “Chemical Kinetics of Ethanol Oxidation”, 2 nd European Combustion Workshop, Louvain-la-Neuve, Belgium, April 3-6, 2005. Poster R15-019.
21	(with S. Skokov, and A. Kazakov), “A Theoretical Study of Oxidation of Phenoxy and Benzyl Radicals by HO ₂ ”, Joint U.S. Sectional Meeting of the Combustion Institute, Drexel University, Philadelphia PA, March, 2005. Paper C22
22	(with Z. Zhao, J. Li, and A. Kazakov), “Thermal Decomposition Reaction and a High Temperature Kinetic Model of Dimethyl Ether”, Joint U.S. Sectional Meeting of the Combustion Institute, Drexel University, Philadelphia PA, March, 2005. Paper C14
23	(with Z. Zhao, J. Li, and A. Kazakov), “Temperature-Dependent Feature Sensitivity Analysis for Combustion Modeling”, Annual National Meeting of the American Chemical Society, Philadelphia PA, August 22-25, 2004 (Poster Presentation)
24	(with J. Li, Z. Zhao, and A. Kazakov), “Comprehensive Kinetic Mechanisms For C ₁ Species Combustion”, 30 th International Symposium on Combustion, Chicago, IL, July 26-31, 2004. Poster IF1-04.

25	(with Z. Zhao [*] , J. Li, and A. Kazakov) “Temperature-Dependent Feature Sensitivity Analysis of Flames”, 30 th International Symposium on Combustion, Chicago, IL, July 26-31, 2004. Poster <i>1F2-13</i> .
26	(with J. Li, Z. Zhao, and A. Kazakov), “An Updated Comprehensive Kinetics Model of H ₂ Combustion”, Eastern States Section: The Combustion Institute Fall Technical Meeting, Penn State University, University Park, PA October 26-29, 2003. Extended Abstract
27	(with L. Zheng and A. Kazakov) “Propene Oxidation Study In a Variable Pressure Flow Reactor”, Eastern States Section: The Combustion Institute Fall Technical Meeting, Penn State University, University Park, PA October 26-29, 2003. Extended Abstract
28	(with J. Li, and A. Kazakov) “Rate Constants of Ethanol Thermal Decomposition”, Eastern States Section: The Combustion Institute Fall Technical Meeting, Penn State University, University Park, PA October 26-29, 2003. Extended Abstract
29	(with Z. Zhao, J. Li, K. Kroenlein, A. Kazakov, and S. P. Zeppieri), “Study of n-Decane/Air Laminar Flame Speed with Mixture Preheating and N ₂ Dilution”, Western States Section/Combustion Institute 2003 Fall Meeting, University of California, Los Angeles, Oct. 20, 21, 2003. Full paper
30	(with J. Li, and A. Kazakov), “Experimental and Numerical Studies of Ethanol Oxidation”, Western States Section/Combustion Institute 2003 Fall Meeting, University of California, Los Angeles, Oct. 20, 21, 2003 Paper No. <i>03F-60</i>

Appendix C - Archival Papers in Review and Pre-prints in Preparation for Archival Review

(with J. Li, A. Kazakov, and M. Chaos), “Chemical Kinetics of Ethanol Oxidation”, 5th US Combustion Meeting, University of California at San Diego, San Diego, CA, March 25-28, 2007. Paper C-26.

(with S. Dooley, M.P. Burke, M. Chaos, Y. Stein, F.L. Dryer, V.P. Zhukov, O. Finch, C.A. Daly, J.M. Simmie, H.J. Curran), *Methyl Formate Oxidation*, 2009. (Archival Manuscript in Preparation)

(with M. Chaos), “Chemical-Kinetic Modeling of Ignition Delays: Considerations in Interpreting Shock Tube Data”, *Int. J. Chemical Kinet.* (Submitted and Accepted with Revisions) July 2008.

(with M. Chaos, M. P. Burke, and Y. Ju), “Syngas Chemical Kinetics and Reaction Mechanisms”, Chapter 2 in *Syngas Combustion*, (Editors: Tim C. Lieuwen, Vigor Yang, Richard A. Yetter), Elsevier, (2009). In Press.

(with F. M. Haas and M. Chaos), “Low and Intermediate Temperature Oxidation of Ethanol and Ethanol-PRF Blends: An Experimental and Modeling Study”, *Combust and Flame*. (Submitted and Pending Revisions)

5th US Combustion Meeting
Organized by the Western States Section of the Combustion Institute
and Hosted by the University of California at San Diego
March 25-28, 2007.

Chemical Kinetics of Ethanol Oxidation

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Experimental profiles of stable species mole fractions are reported for ethanol oxidation in a Variable Pressure Flow Reactor (VPFR) at initial temperatures of 800-950K, constant pressures of 3 to 12atm, and equivalence ratios from 0.3 to 1.4. A detailed mechanism for ethanol combustion is developed in a hierarchical manner. Each kinetic subset comprising the present mechanism was tested by thorough comparison of model predictions and experimental results found in laminar premixed flames, shock tubes, and flow reactors [Li, PhD thesis (2004); Li et al. *International Journal of Chemical Kinetics* 39 (2007) 109-136]. In this study, the assembled mechanism is further tested against the ethanol oxidation data collected in the VPFR as well as shock-tube ignition data, laminar burning velocities, and structures of counterflow diffusion and partially premixed flame available in the literature. The present ethanol mechanism performs well against this wide ranging set of data and shows a significant improvement of predictions of the newly collected VPFR data over results obtained using other recently published mechanisms [N.M. Marinov, *International Journal of Chemical Kinetics* 31 (1999) 183-220; P. Saxena, F.A. Williams, *Proceedings of the Combustion Institute* 31 (2007) 1149-1156].

1. Introduction

Ethanol (C₂H₅OH) is a very important energy carrier that can be produced from renewable energy resources. It can be used as a fuel extender, octane enhancer, and oxygen-additive in, or as an alternative, neat fuel to replace reformulated gasoline. Ethanol also has potential as a hydrogen carrier for fuel cell applications. The 1990 Clean Air Act Amendments [1] presently require the addition of oxygenates to reformulated gasoline, with seasonal adjustments, on the premise that oxygen content decreases automotive emissions, particularly smog generation participants and carbon monoxide. Ethanol is favored to replace methyl tertiary butyl ether (MTBE), another widely used oxygenate additive that has become unpopular based upon ground water contamination and human health effects. While most ethanol is currently generated by fermentation (grain alcohol), recent developments suggest that ethanol fuel can be derived more efficiently from other biomass, thus offering potential to reduce dependence on fossil fuel energy resources.

The chemistry of gas-phase oxidation and pyrolysis of ethanol have been the subjects of numerous studies over the last five decades. Data have been reported from shock tubes, static

reactors, flow reactors, diffusion flames, and laminar premixed flame experiments. Norton and Dryer [2] conducted a series of ethanol oxidation experiments in an Atmospheric Pressure Flow Reactor (APFR). In the modeling efforts of Norton and Dryer, as well as those of several other investigators [3-5] the importance of including all three isomeric forms of C_2H_5O produced by H-atom abstraction from ethanol was emphasized. Marinov [6] carried out an extensive detailed kinetic modeling study of ethanol combustion at intermediate and high temperatures. His computational results indicated that ethanol oxidation exhibits strong sensitivity to branching ratio assignments of the H-atom abstraction reactions of ethanol as well as to the kinetics of its uni-molecular decomposition. The mechanism performed reasonably well under the experimental conditions found in laminar premixed flames, shock tubes, and the APFR. More recently, Saxena and Williams [7] developed an ethanol mechanism by extending prior kinetic efforts on small hydrocarbon chemistry (i.e. their evolving “San Diego Mechanism” [8]). The ethanol subset of reactions added to their earlier work was taken initially from work developed in our laboratory [9, 10], on which the present study is based. Saxena and Williams [7] measured species profiles in counterflow flames and published comparisons of their model against their data as well as published shock tube ignition delay, burning velocity, and extinction measurements, claiming superiority of the predictive nature of their model against their experiments in comparison to that found using the kinetic model developed in [9], and discussed below. However, no model comparisons against pyrolysis and high-pressure oxidation characteristics of ethanol at flow reactor conditions found in [9] were presented, which include data from which new rate determinations for ethanol uni-molecular decomposition reactions were obtained [11, 12].

We noted in earlier publications [9-12] that ethanol uni-molecular decomposition is important (as also observed by Marinov [6]), even under oxidation conditions at temperatures found in the flow reactor as well as other combustion systems. Uncertainties in the uni-molecular decomposition reactions of ethanol, and branching ratio assignments of the H-atom abstraction reactions by H and CH_3 radicals are such that these reactions must be collectively considered if ethanol pyrolysis is to be predicted well. Upon this validation result, the selection of other abstraction reaction channels and branching ratios relevant to oxidative conditions must be considered in light of the parameter combinations used for modeling pyrolysis. We found that the model of Marinov [6] would not predict pyrolysis data [11], principally because of the assigned rates for the uni-molecular decomposition channels and subsequent impact of the selection of abstraction channel parameters and branching ratios. Hence, its predictions of oxidation results were also compromised, as shown below. As a result, we set about developing a new comprehensive pyrolysis and oxidation model and to also develop a broader set of pyrolysis and oxidation flow reactor validation data.

We first studied the uni-molecular decomposition channels of ethanol, deriving new parameters from radical trapping experiments [12], then developed the abstraction reaction parameter and branching sub model components important to predicting pyrolysis experiments. Subsequently, a full model was developed to predict ethanol pyrolysis and oxidation observations. The pyrolysis results have been extensively discussed in the literature previously [11, 12]. The present paper reports in a comprehensive manner new flow reactor data for ethanol oxidation at high-pressure conditions (3-12 atm) with initial temperatures of 800-950K and equivalence ratios ranging from 0.6 to 1.4 and discusses the oxidation model development and performance, detailed in [9] and briefly summarized earlier in [10]. Here we briefly describe the hierarchical development of the present model and compare predictions against a wide range of experimental

data, including the present high-pressure flow reactor results, shock tube ignition delay data, and flame measurements. We also present for the first time predictions using the recent mechanism of Saxena and Williams [7] against our flow reactor oxidation data. These model predictions are inferior to those generated using the present model.

2. Experimental Methods

Experiments were conducted in the Princeton Variable Pressure Flow Reactor (VPFR). A schematic of the flow reactor is shown in Figure 1. Detailed information about the VPFR instrumentation and experimental methodology can be found in other publications [12, 13], and only a brief description of these issues is given here.

Carrier gas (N_2 in this study) is heated by a pair of electrical resistance heaters and directed into a reactor duct. Oxygen is also introduced at the duct entrance. The carrier gas/oxygen mixture flows around a baffle plate into a gap serving as the entrance to a diffuser. The vaporized fuel (ethanol) flows into the center tube of a fuel injector, and injected radially outward into the gap where it rapidly mixes with the carrier gas and oxygen. The reacting mixture exits the diffuser into a constant area test section. Near the exit of the test section, a sampling probe is positioned on the reactor centerline to continuously extract and convectively quench a small portion of the flow. At the same axial location, the local gas temperature is measured with a type R thermocouple accurate to ± 3 K.

The sample gas flows via heated Teflon lines to analytical equipment including a Fourier transform infrared spectrometer (FTIR), an electrochemical O_2 analyzer, and a pair of non-dispersive infrared analyzers for CO and CO_2 . The majority of the stable species of interest (C_2H_5OH , H_2O , C_2H_4 , CH_4 , CH_3CHO , etc.) are measured continuously on-line using FTIR spectrometry. The measurement uncertainties for the data reported here are: O_2 - $\pm 2\%$, CO - $\pm 2\%$, CO_2 - $\pm 2\%$, C_2H_5OH - $\pm 3\%$, H_2O - $\pm 6\%$, C_2H_4 - $\pm 3\%$, CH_4 - $\pm 4\%$, CH_3CHO - $\pm 3\%$, CH_2O - $\pm 3\%$, C_2H_6 - $\pm 4\%$, and C_2H_2 - $\pm 3\%$ of reading. Additional species can be determined using discrete gas samples acquired from the sample flow and off-line gas chromatographic analyses.

The distance between the point of fuel injection and the sampling position is varied by moving the fuel vapor injector probe (with attached mixer/diffuser assembly), relative to the fixed sampling location. Mean axial velocity measurements along the centerline of the reactor are used to correlate distance with residence time. In this way, profiles of stable species versus the residence time can be determined experimentally. The uncertainty in the reported residence times is approximately 5%.

A series of species-time history ethanol oxidation (C_2H_5OH/O_2 in balance N_2) experiments were conducted in the VPFR at initial temperatures of 800-950K, pressures of 3-12 atm, equivalence ratios of 0.6-1.4, and a fixed initial C_2H_5OH molar concentration of 0.3%. In all of the experiments, the total carbon and oxygen balances experimentally determined at each residence time were within 5% of the specified input. The steady total carbon and oxygen concentrations at each sampling location not only provide verification of the experimental measurements, but also imply that any other carbon- or oxygen-containing stable species are present in negligible quantities. This result was also verified by off-line gas chromatographic analyses.

Figure 1: Schematic of the variable pressure flow reactor (VPFR).

3. Chemical Kinetics Model

Predictions using the ethanol mechanisms of Marinov [6] and Saxena and Williams [7] are compared with the present experimental data for two representative cases at 3 and 9 atm in Figs. 2 and 3. The model predictions are compared to the experimental measurements by shifting the simulated values along the time axis to match the 50% fuel consumption point. The predicted fuel and oxygen consumption rates, as well as the production rates of major intermediates, such as H_2O , CH_4 , and C_2H_4 are substantially different from the experimental results, independent of any time shifting considerations. Predictions from the model of Saxena and Williams [7] are reasonable for the lower pressure case (Fig. 3a); however they deteriorate as pressure increases (Fig. 3b). In fact, at 9 atm a positive time shift is required to match the experimental 50% fuel consumption location, which is unphysical and usually indicates that the induction time is under predicted by the model even without consideration of mixing effects. Saxena and Williams [7] adopted rate parameters for ethanol decomposition and abstraction reactions directly from [9] (the basis of the present work). This indicates that the source of the discrepancy is not incorrect initiation and branching ratio assignments, shown to be highly coupled in ethanol pyrolysis experiments [11, 12] and points to deficiencies at the lower molecular level.

The detailed pyrolysis and oxidation model reported here consists of 39 species and 238 reversible elementary reactions and was developed in a *comprehensive, hierarchical* manner. The combustion of hydrocarbon species follows a basic series of steps, beginning with initiation decomposition reactions, followed by radical attack on the fuel, production of generally smaller intermediates, and finally a chain of aldehyde $\rightarrow \text{CO} \rightarrow \text{CO}_2$ steps. In the above process, the radical pool responsible for chain propagation, branching, and termination is mainly determined by the H_2/O_2 reaction mechanism. By taking these basic steps in the reverse order, the detailed mechanism was built hierarchically. The present ethanol mechanism development initially involved further consideration of the H_2 oxidation sub-mechanism, followed by C_1 sub-mechanism including CO , CH_2O , CH_3OH , and CH_4 combustion, then the C_2 sub-mechanism components including the reactions for C_2H_X ($X = 1-6$), CH_3CHO , and $\text{C}_2\text{H}_5\text{OH}$. The hierarchy of the development of the ethanol chemical kinetics model is shown in Fig. 4.

Figure 2: Oxidation of $C_2H_5OH/O_2/N_2$ mixtures in the VPFR. Initial conditions: a) $P = 3$ atm, $T = 950$ K, 0.3 % C_2H_5OH concentration, $\phi = 1.2$; b) $P = 9$ atm, $T = 830$ K, $X_{C_2H_5OH} = 0.3\%$, $\phi = 1$. Symbols are present experimental measurements, lines are modeling predictions using the mechanism of Marinov [6]; dashed lines correspond to open symbols. Predictions have been shifted by -0.17 s (a) and -0.88 s (b).

At each level, the newly added portions of the mechanism were tested and validated by thorough comparison with experimental data over wide ranges of physical conditions for the sub-mechanism species. These experimental sources included laminar flame speeds, shock tube ignition delay data, flow reactor measurements, and other sources such as observations in static and stirred reactors. In conjunction with sensitivity and reaction flux analyses, the selected starting sub-mechanisms (H_2/O_2 mechanism of Mueller et al. [14], CH_3OH/O_2 mechanism of Held and Dryer [15], and C_2H_5OH/O_2 mechanism of Marinov [6]), were updated and/or revised to reflect recent publications of thermodynamic data, rate coefficients, and channel results. Detailed information of each level of the present ethanol mechanism development can be found elsewhere [9, 16]. A brief summary of important considerations is presented below.

H_2/O_2 sub-mechanism. The entire sub-mechanism was replaced with our recent updated version [17] of that published earlier by Mueller et al. [14]. The revised mechanism encompasses recently published thermodynamic data for OH and rate constants for two important reactions: $H + O_2 = OH + O$ [18] and $H + O_2 (+M) = HO_2 (+M)$ [19]. Sensitivity analyses show that the reaction $H + OH + M = H_2O + M$ is of significance to the observations in high-pressure flame propagation. Its rate constant was modified within known uncertainty limits to achieve flame propagation model performance.

Figure 3: Oxidation of $C_2H_5OH/O_2/N_2$ mixtures in the VPFR. Initial conditions: a) $P = 3$ atm, $T = 950$ K, 0.3% C_2H_5OH concentration, $\phi = 1.2$; b) $P = 9$ atm, $T = 830$ K, $X_{C_2H_5OH} = 0.3\%$, $\phi = 1$. Symbols are present experimental measurements, lines are modeling predictions using the mechanism of Saxena and Williams [7]; dashed lines correspond to open symbols. Predictions have been shifted by -30 ms (a) and $+50$ ms (b).

Figure 4: Hierarchical structure of the present ethanol oxidation mechanism.

CO, CH_2O , CH_3OH/O_2 sub-mechanism. The C_1 sub-mechanism was developed based on the CH_3OH/O_2 mechanism of Held and Dryer [15]. Recently, kinetic parameters for CH_3 , HCO , and CH_2O related reactions as well as new experimental data for C_1 species have become available. The CO/O_2 , CH_2O/O_2 , and CH_3OH/O_2 mechanisms were revisited, considering the new kinetic information. The most important revisions to the original model involve the rate constant

descriptions for the reactions $\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$ and $\text{HCO} + \text{M} = \text{H} + \text{CO} + \text{M}$. Recent theoretical calculations of the rate constant of $\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$ predict values higher than experimental measurements at low to intermediate temperatures [16]. The temperature-dependent sensitivity analysis of Zhao et al. [20] demonstrates that flame speeds of hydrocarbons are most sensitive to the value of the rate constant of $\text{HCO} + \text{M} = \text{H} + \text{CO} + \text{M}$ at 1300–2000K, well above the range of conditions of the recently published measurement for this reaction. After an exhaustive literature review, Li et al. [16] performed weighted least square fits on the entire body of experimentally measured rate constants for these two reactions yielding the following expressions:

$$k_{\text{CO}+\text{OH}=\text{CO}_2+\text{H}} = 2.23 \times 10^5 T^{1.89} \exp\left(\frac{583}{T}\right) \quad k_{\text{HCO}+\text{M}=\text{H}+\text{CO}+\text{M}} = 4.75 \times 10^{11} T^{0.66} \exp\left(-\frac{7485}{T}\right)$$

Further description of the C_1 sub-mechanism, including its validation against a wide range of experimental data can be found in Ref. 16. Since the initial development of the mechanism, recent works [21–23] suggest that the reaction parameters for the reaction $\text{CO} + \text{HO}_2 = \text{CO}_2 + \text{H}$ are substantially less than originally recommended by Mueller et al. [14]. More detailed discussions pertaining to this issue appear in Ref. 16. The substitution of these new rate parameters into the C_1 sub-mechanism have no significant effect on any of the predictions reported here.

$\text{C}_2\text{H}_X/\text{O}_2$ sub-mechanism. The C_2H_X ($X = 1-6$), as well as CH_2 and HCCO sub-models were primarily taken from the C_2 chemistry of Wang et al. [24], which was derived from the GRI-1.2 mechanism [25]. Wang et al. [24] tested their mechanism against a variety of C_2H_2 and C_2H_4 experiments, including ignition behavior, laminar flame propagation, and detailed structure of burner-stabilized flames, and the mechanism was demonstrated to reproduce most of the experiment results.

$\text{CH}_3\text{CHO}/\text{O}_2$ sub-mechanism. Acetaldehyde combustion chemistry, including CH_3CHO , CH_3CO , CH_2CHO , and CH_2CO reactions, was based on the sub-mechanism appearing in Marinov [6]. All acetaldehyde mechanisms currently available in literature (e.g. [6, 26, 27]) failed to give reasonable predictions of acetaldehyde experiments previously conducted in the VPFR [28]. The discrepancy makes clear that considerable work remains to reconcile predictions with experimental measurements. Here we made revisions to elementary acetaldehyde reactions based on an extensive literature review, especially for decomposition as well as abstraction reactions involving OH. Further studies on the acetaldehyde decomposition and abstraction reactions with other radicals, like HO_2 , are continuing.

$\text{C}_2\text{H}_5\text{OH}/\text{O}_2$ sub-mechanism. The ethanol subset consists of ethanol decomposition reactions, abstraction reactions generating three isomeric forms of $\text{C}_2\text{H}_5\text{O}$ due to the three possible sites for H-atom abstraction in $\text{C}_2\text{H}_5\text{OH}$ molecules, and subsequent reactions of $\text{C}_2\text{H}_5\text{O}$ to produce C_1 or other C_2 species whose mechanism has been established above. The current ethanol sub-mechanism was based on that of Marinov [6] with revisions to ethanol decomposition and abstraction reactions. The fall-off kinetics of ethanol decomposition was described by our recent study based on pyrolysis experiments [11] with radical trappers and RRKM/master equation calculations [12]. Extensive literature review of ethanol abstraction reactions shows there are very few elementary experimental measurements available. In the present study, the rate constants of abstraction reactions were modified to better reproduce the VPFR experiments [9].

Thermodynamic data. The thermodynamic properties of species found in the detailed mechanism were primarily obtained from the CHEMKIN thermodynamic database [29] and Burcat's thermochemical database [30], except for OH, HO₂, and CH₂OH. The standard heats of formation of OH and HO₂ at 298 K were updated to 8.9 kcal/mol [31] and 3.0 kcal/mol [32], respectively. Recently, Ruscic et al. [33] have updated the heat of formation for HO₂ to 2.94 ± 0.06 kcal/mol. This change makes no significant difference in the quality of predictions obtained in the present work, for our laboratory has consistently used a heat of formation for HO₂ within the uncertainties of the now accepted value in all of our previous modeling studies. The thermochemical properties of CH₂OH, including enthalpy of formation, standard entropy, and heat capacity at different temperatures, were taken from [34] and agree with the recent evaluation of Ruscic et al. [35].

4. Results and discussion

The ethanol mechanism described above was compared against the expansive set of VPFR experiments performed in this study. The combined results are shown in Figs. 5-8. The predictions of the major stable species (C₂H₅OH, O₂, H₂O, CO, and CO₂) using the present mechanism agree very well with the experimental measurements and represent a significant improvement over predictions using the mechanisms of Marinov [6] and Saxena and Williams [7] (see Figs. 2 and 3). For other stable species, the model predictions are reasonable but can be further improved, especially at higher pressures. Mechanistic elements, particularly those involving acetaldehyde and its reactive intermediates, remain under consideration in further improving the present version of the ethanol oxidation mechanism. The quality of predictions of the present mechanism for the atmospheric pressure flow reactor data of Norton and Dryer [2] is similar to that shown in Figs. 5-8. Clearly ethanol pyrolysis calculations are also in very good agreement with the experiments of Li et al. [11] as the uni-molecular decomposition rates used in the present mechanism were adopted from that study.

Figure 5: Time evolution of stable major (left) and minor intermediate (right) species during VPFR oxidation of $C_2H_5OH/O_2/N_2$ mixtures at 3 atm, initial temperature of 950 K, and initial molar fuel concentration of 0.3 %: top – $\phi = 0.6$; middle – $\phi = 1.0$; bottom – $\phi = 1.2$. Symbols are experimental measurements; lines are predictions from the present model. Dashed lines correspond to open symbols. Computed profiles have been shifted by -98 ms (top), -110 ms (middle), and -106 ms (bottom).

Figure 6: Time evolution of stable major (left) and minor intermediate (right) species during VPFR oxidation of $C_2H_5OH/O_2/N_2$ mixtures at 6 atm, initial temperature of 860 K, and initial molar fuel concentration of 0.3 %: top – $\phi = 0.6$; middle – $\phi = 1.0$; bottom – $\phi = 1.2$. Symbols are experimental measurements; lines are predictions from the present model. Dashed lines correspond to open symbols. Computed profiles have been shifted by -0.40 s (top), -0.35 s (middle), and -0.35 s (bottom).

Figure 7: Time evolution of stable major (left) and minor intermediate (right) species during VPFR oxidation of $\text{C}_2\text{H}_5\text{OH}/\text{O}_2/\text{N}_2$ mixtures at 9 atm, initial temperature of 830 K, and initial molar fuel concentration of 0.3 %: top – $\phi = 0.6$; middle – $\phi = 1.0$; bottom – $\phi = 1.4$. Symbols are experimental measurements; lines are predictions from the present model. Dashed lines correspond to open symbols. Computed profiles have been shifted by -0.66 s (top), -0.65 s (middle), and -0.60 s (bottom).

Figure 8: Time evolution of stable major (left) and minor intermediate (right) species during VPFR oxidation of $C_2H_5OH/O_2/N_2$ mixtures at 12 atm, initial temperature of 800 K, and initial molar fuel concentration of 0.3 %: top – $\phi = 0.6$; middle – $\phi = 1.0$; bottom – $\phi = 1.4$. Symbols are experimental measurements; lines are predictions from the present model. Dashed lines correspond to open symbols. Computed profiles have been shifted by -1.20 s (top), -1.10 s (middle), and -1.08 s (bottom).

The present ethanol mechanism was also tested against experimental observations found in shock tubes, laminar premixed flames, and counterflow flames. The SENKIN [36], PREMIX [37], and OPPDIF [38] codes were used for ignition delay, laminar burning velocity, and counterflow flame calculations, respectively. The standard CHEMKIN transport package was used for the counterflow as well as burning velocity calculations with Soret effects and multi-component diffusion included. The resolution of imposed grids was such that fully converged solutions were obtained for both PREMIX and OPPDIF calculations.

Ignition of $\text{C}_2\text{H}_5\text{OH}/\text{O}_2/\text{Ar}$ mixtures has been studied behind reflected shock waves by Natajara and Bhaskaran [3], Dunphy et al [4, 5], and Curran et al. [39]. Experiments spanned temperatures of 1100 to 1700 K, pressures of 1 to 4.5 atm, and equivalence ratios of 0.25 to 2.0. Figure 9 presents results of calculated ignition delays using the present mechanism compared against the data of Natajara and Bhaskaran [3] and Curran et al. [39]; reasonable agreement is shown. The model captures the experimentally observed insensitivity of ignition delay to changes in stoichiometry (Fig. 9a). For the higher pressure experiments of Curran et al. [39], the model predictions exhibit a similar pressure dependence as that seen experimentally but overpredict the overall activation energy (Fig 9b).

Figure 9: Ignition delays of $\text{C}_2\text{H}_5\text{OH}/\text{O}_2/\text{Ar}$ mixtures in a shock tube. a) Model comparisons against data of Natajara and Bhaskaran [3] at 1.43% ($\phi = 0.5$), 2.5% ($\phi = 1.0$), and 4.0% ($\phi = 2.0$) initial $\text{C}_2\text{H}_5\text{OH}$ molar concentration. Results for $P = 2$ atm have been reduced by half for clarity; b) Model comparisons against data of Curran et al [39] at stoichiometric conditions and an initial molar fuel concentration of 2.5%. Symbols are experimental data with lines showing prediction using the present model. Dashed lines correspond to open symbols.

Figure 10 compares predicted laminar burning velocities against the measurements of Gülder [40] and Egolfopoulos et al. [41]. The measurements were performed in different experimental devices (i.e. a spherical bomb [40] and counterflow burner [41]) at pressures up to 8 atm [41] and initial temperatures up to 453 K [41]. Good agreement is observed in Fig. 10 for atmospheric flames at all temperatures considered. The model also predicts well the burning velocity at elevated pressures.

Figure 10: Laminar burning velocities of ethanol/air mixtures. Open symbols correspond to the measurements of Egolfopoulos et al. [41] at atmospheric pressure; other symbols are the measurements of Gülder [40]. Lines are predictions of the present model.

Figure 11: Species and temperature profiles of ethanol partially premixed (left) and diffusion (right) counterflow flames. Symbols are measurements of Saxena and Williams [7], lines are present model predictions. Dashed lines correspond to open symbols.

Saxena and Williams [7] performed experiments on flame structures using a counterflow burner. Measurements were performed on both partially premixed and diffusion systems at a strain rate of 100 s^{-1} . The study of Saxena and Williams [7] has recently appeared in the open literature and the measurements reported present an opportunity to test present model predictions against new

data not utilized in its development. Figure 11 shows the results of the flame measurements [7] against calculations using the present mechanism. Very good agreement can be observed for the major species. There is a slight overprediction of the combined concentration of ethylene and acetylene and both methane and ethane are underpredicted by nearly 35% and 50% respectively. The quality of predictions from the present mechanism is comparable to that obtained by Saxena and Williams [7] using their model except for methane which was better predicted. This result can be explained by the lower rate chosen in [7] for methyl radical recombination relative to that used in the present model, which leads to higher methane production by the channeling of methyl radicals through $\text{CH}_3 + \text{H}$ recombination. In the present mechanism the latest update to the $\text{CH}_3 + \text{CH}_3 = \text{C}_2\text{H}_6$ reaction is used [43] and it is noted that Saxena and Williams [7] employ a dated value [44]. Nonetheless, increasing the rate of H abstraction by methyl from ethanol by a factor of 2 would bring methane predictions within experimental uncertainty whereas only altering flow reactor methane profiles (Fig. 5-8) by 15%. As discussed by Saxena and Williams [7] the discrepancy between measured and predicted ethane profiles may be removed by decreasing the rate of the reaction $\text{C}_2\text{H}_6 + \text{H} = \text{C}_2\text{H}_5 + \text{H}_2$. It is not our intent in this paper to modify the model described here to better predict the new flame data [7]. To perform such a task would require the re-validation of the model not only for ethanol targets presented here but also for targets used in its development at the lower molecular subsets.

5. Conclusion

Species evolution profiles during the high pressure oxidation of ethanol in a flow reactor have been measured and reported here. Predictions of the new experimental data based upon a previous [6] and a recently published ethanol oxidation mechanism [7] are significantly deficient. The new comprehensive detailed kinetic model developed herein takes advantage of the hierarchical nature of reacting systems, beginning with the H_2/O_2 reaction mechanism [17], and subsequently encompassing C_1/O_2 (thoroughly updated and tested by Li et al. [16]), $\text{C}_2\text{H}_x/\text{O}_2$, $\text{CH}_3\text{CHO}/\text{O}_2$, and $\text{C}_2\text{H}_5\text{OH}/\text{O}_2$ subsets in order of increasing complexity. The relevant mechanism consists of 39 species and 238 reactions. Important updates/modifications to the original ethanol reaction subset (based on the work of Marinov [6]) were made to reflect recent updates of thermodynamic data, rate coefficients, and branching ratios. The present mechanism has been validated by thorough comparison between numerically predicted and experimentally observed results found in laminar premixed flames, shock tubes, counterflow flames, and flow reactors including the experiments reported herein. Predictions are reasonably good for the major species profiles observed in the new VPFR experiments, and significantly improve the agreement with the experimental targets originally investigated by Marinov [6]. No effort has been made to further minimize the dimensional characteristics of the model for predicting specific validation targets. The present study further demonstrates the continual need to re-evaluate any “comprehensive” mechanism [42] as new experimental validation constraints are considered and/or as improved kinetic and thermochemical parameters become available.

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References

1. Energy Information Administration, Alternatives to Traditional Transportation Fuels (1996) DOE/EIA-0585.
2. T.S. Norton, F.L. Dryer, *International Journal of Chemical Kinetics* 24 (1992) 319-344.
3. K. Natarajan, K.A. Bhaskaran, *Thirteenth International Symposium on Shock Waves* (1981) 834-842.
4. M.P. Dunphy, J.M. Simmie, *Journal of the Chemical Society, Faraday Transactions* 87 (1991) 1691-1696.
5. M.P. Dunphy, P.M. Patterson, J.M. Simmie, *Journal of the Chemical Society, Faraday Transactions* 87 (1991) 2549-2560.
6. N.M. Marinov, *International Journal of Chemical Kinetics* 31 (1999) 183-220.
7. P. Saxena, F.A. Williams, *Proceedings of the Combustion Institute* 31 (2007) 1149-1156.
8. <http://www-mae.ucsd.edu/~combustion/cermech/>
9. J. Li, PhD thesis, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ (2004).
10. J. Li, A. Kazakov, F.L. Dryer, European Combustion Meeting, Louvain-la-Neuve, Belgium (2005) Paper 019.
11. J. Li, A. Kazakov, F.L. Dryer, *International Journal of Chemical Kinetics* 133 (2001) 859-867.
12. J. Li, A. Kazakov, F.L. Dryer, *Journal of Physical Chemistry A* 108(2004) 7671-7680.
13. T.J. Held, Ph.D. thesis, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, 1993.
14. M.A. Mueller, T.J. Kim, R.A. Yetter, F.L. Dryer, *International Journal of Chemical Kinetics* 31 (1999) 113-125.
15. T.J. Held, F.L. Dryer, *International Journal of Chemical Kinetics* 30 (1998) 805-830.
16. J. Li, Z. Zhao, A. Kazakov, M. Chaos, F.L. Dryer, J.J. Scire, *International Journal of Chemical Kinetics* 39 (2007) 109-136.
17. J. Li, Z. Zhao, A. Kazakov, F.L. Dryer, *International Journal of Chemical Kinetics* 36 (2004) 566-575.
18. J.P. Hessler, *Journal of Physical Chemistry A* 102 (1998) 4517-4526.
19. J.V. Michael, M.C. Su, J.W. Sutherland, J.J. Carroll, A.F. Wagner, *Journal of Physical Chemistry A* 106 (2002) 5297-5313.
20. Z. Zhao, J. Li, A. Kazakov, F.L. Dryer, *International Journal of Chemical Kinetics* 37 (2004) 282-295.
21. G. Mittal, C.J. Sung, M. Fairweather, A.S. Tomlin, J.F. Griffiths and K.J. Hughes, *Proceedings of the Combustion Institute* 31 (2007) 419-427.
22. R. Sivaramakrishnan, A. Comandini, R.S. Tranter, K. Brezinsky, S.G. Davis and H. Wang, *Proceedings of the Combustion Institute* 31 (2007) 429-437.
23. H. Sun, S.I. Yang, G. Jomaas and C.K. Law, *Proceedings of the Combustion Institute* 31 (2007) 439-446.
24. H. Wang, A. Laskin, Z.M. Djuricic, C.K. Law, S.G. Davis, D.L. Zhu, Fall Technical Meeting of the Eastern States Section of the Combustion Institute, Raleigh, NC, pp. 129-132 (1999).
25. M. Frenklach, H. Wang, M. Goldenberg, G.P. Smith, D.M. Golden, C.T. Bowman, R.K. Hanson, W.C. Gardiner, V. Lissianski, GRI Technical Report No. GRI-95/0058 (1995).
26. A.A. Borisov, V.M. Zamanskii, A.A. Konnov, V.V. Lisyanskii, S.A. Rusakov, G.I. Skachkov, *Soviet Journal of Chemical Physics* 4 (1989) 2561-2537.
27. P. Dagaut, M. Reuillon, D. Voisin, M. Cathonnet, M. McGuinness, J.M. Simmie, *Combustion Science and Technology* 107 (1995) 301-316.
28. D.C. Zarubiak, M.S.E. Thesis, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ (1997).
29. R.J. Kee, F.M. Rupley, J.A. Miller, Sandia National Laboratories Report No. SAND87-8215 (1987).
30. <ftp://ftp.technion.ac.il/pub/supported/aetdd/thermodynamics> (2007).
31. B. Ruscic, A.F. Wagner, L.B. Harding, R.L. Asher, D. Feller, D.A. Dixon, K.A. Peterson, Y. Song, X. Qian, C. Ng, J. Liu, W. Chen, D.W. Schwenke, *Journal of Physical Chemistry A* 106 (2002) 2727-2747.
32. A.J. Hills, C.J. Howard, *Journal of Chemical Physics* 81 (1984) 4458-4465.
33. B. Ruscic, R.E. Pinzon, M.L. Morton, N.K. Srinivasan, M.-C. Su, J.W. Sutherland, J.V. Michael, *Journal of Physical Chemistry A* 110 (2006) 6592-6601.
34. R.D. Johnson III, J.W. Hudgens, *Journal of Physical Chemistry* 100 (1996) 19874-19890.

35. B. Ruscic, J.E. Boggs, A. Burcat, A.G. Csaszar, J. Demaison, R. Janoschek, J.M.L. Martin, M.L. Morton, M.J. Rossi, J.F. Stanton, P.G. Szalay, P.R. Westmoreland, F. Zabel, T. Berces, *Journal of Physical and Chemical Reference Data* 34 (2005) 573-656.
36. A.E. Lutz, R.J. Kee, J.A. Miller, Technical Report SAND87-8248, Sandia National Laboratories (1987).
37. R.J. Kee, J.F. Grcar, M.D. Smooke, J.A. Miller, Technical Report SAND85-8240, Sandia National Laboratories (1985).
38. A.E. Lutz, R.J. Kee, J.F. Grcar, F.M. Rupley, Technical Report SAND96-8243, Sandia National Laboratories (1996).
39. H.J. Curran, M.P. Dunphy, J.M. Simmie, C.K. Westbrook, W.J. Pitz, *Proceedings of the Combustion Institute* 24 (1992) 769-776.
40. O.L. Gülder, *Proceedings of the Combustion Institute* 19 (1982) 275-281.
41. F.N. Egolfopoulos, D.X. Du, C.K. Law, *Proceedings of the Combustion Institute* 24 (1992) 833-841.
42. C.K. Westbrook, F.L. Dryer, *Combustion Science and Technology* 20 (1979) 125-140.
43. B. Wang, H. Hou, L.M. Yoder, J.T. Muckerman, C. Fockenberg, *Journal of Physical Chemistry A* 107 (2003) 11414-11426.
44. J.C. Hewson, F.A. Williams, *Combustion and Flame* 117 (1999) 441-476.

Methyl Formate Oxidation

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Abstract

The oxidation of methyl formate (CH_3OCHO) has been studied in three experimental apparatuses over a range of combustion relevant conditions;

- (1) in a variable-pressure flow reactor at 3 atm, 900 K, 0.5% fuel concentration, and at stoichiometries of 0.5, 1.0 and 1.5. Reactant, major intermediate and product species have been quantified as a function of residence time.
- (2) a shock tube has been used to measure the autoignition of $\text{CH}_3\text{OCHO}/\text{O}_2/\text{Ar}$ mixtures at pressures of ≈ 2.7 , 5.4 and 9.4 atm and temperatures of 1275–1935 K for mixture compositions of 0.5% fuel at equivalence ratios of 1.0, 2.0 and 0.5 and 2.5% fuel at an equivalence ratio of 1.0.
- (3) a pressure-release type high-pressure chamber has been used to measure the laminar burning velocities of outwardly propagating spherical $\text{CH}_3\text{OCHO}/\text{air}$ flames at atmospheric pressure for stoichiometries ranging from 0.8–1.6.

A detailed chemical kinetic model has been constructed and used to explain these experimental data by means of model validation. The kinetic model shows methyl formate oxidation to proceed through a balance between concerted elimination reactions, principally forming methanol and carbon monoxide and bimolecular hydrogen abstraction reactions. The extent of each mechanism of oxidation was found to depend on the particular environment but in general, the shock tube study shows methyl formate to be consumed exclusively unimolecularly, while the flow reactor

and freely propagating flame studies show competition between hydrogen abstraction from fuel and concerted elimination as the main mechanism of methyl formate oxidation.

Key words: methyl formate, methyl ester, biofuel, biodiesel, oxidation, shock tube, flow reactor, combustion, modeling, autoignition, DME, DMM, burning velocity

1 Introduction

There has been recent interest in studying various oxygenated fuels for their ability to reduce the emission of CO, NO_x, particulates and non-methane hydrocarbons from diesel engines. Dimethyl ether (DME) and dimethoxy methane (DMM) are two of the fuels that have been proposed to either replace totally or be blended with conventional diesel fuel to reduce particulate emissions. Emissions are reduced, apparently, primarily by a reduction in the formation of particulates rather than an increased rate of *in situ* particulate oxidation. By reducing particulate emissions at a certain operating condition, other adjustments in diesel operating parameters (specifically injection timing and exhaust gas recirculation) can be made to reduce NO_x emissions. Thus the use of these oxygenated fuels relaxes the typical particulate/NO_x trade-off constraints normally found in using conventional diesel fuels. The major intermediate formed in the oxidation of DMM is methyl formate (MF) [1, 2] and although MF is also a major intermediate in the oxidation of DME in the presence of NO_x as shown by Liu et al [3], it appears to be only a minor species of little importance in the pure oxidation reaction, particularly at high temperatures. MF has also been shown to be a significant intermediate in the atmospheric oxidation of DME [4]. For these practical reasons the oxidation of MF is of special interest.

Secondly, methyl esters of varying alkyl chain length are the primary constituent of biodiesel [5]. MF represents the basic methyl ester and as such its study allows for the isolation of the role of the ester functionality on combustion processes. For this reason MF has been the subject of two previous kinetic modeling studies. In 2000 Fisher et al. [6] constructed detailed kinetic models for the oxidation of MF and its n-alkyl cousin, methyl butanoate. However it was not until 2009 that appropriate experimental data on MF oxidation was available with which to perform model validation; Westbrook et al. [7] have recently studied the fuel-rich oxidation of MF as one of a series of esters in very low pressure (≈ 25 Torr) burner stabilized flames, their submechanism for MF oxidation was able to satisfactorily reproduce the measured major species from within the flame.

The chemical mechanism of MF decomposition has been the subject of several

experimental and computational investigations. Although all agree that the process is generally unimolecular there is some debate over the precise mechanism. Davis [8] studied MF decomposition using a shock tube and observed large amounts of methanol to be formed. These measurements have been taken as proof of the decomposition pathway of MF suggested by Steacie;

Jain and Murwaha [10] agree that MF decomposition occurs in a concerted fashion and does not involve radical chain reactions. However they suggest that MF decomposes to produce two molecules of formaldehyde via the isomerization of the exotic carbene species, hydroxymethylene;

In a 0.5–10 Torr study of MF dissociation using a multiphoton excitation technique Periera and Isolani [11] observed large amounts of methanol and carbon monoxide together with smaller amounts of methane, carbon dioxide and ethane. These authors take the production of ethane as evidence of C—O lysis producing $\dot{\text{C}}\text{H}_3$ radical, which may recombine to produce the observed ethane concentrations. They suggest that these products may be accounted for by the scheme proposed by Steacie.

Like Davis [8], Steacie [9] and Jain and Murwaha [10], Francisco [12] studied the gas phase decomposition of MF but with modern computational techniques. *Ab initio* molecular orbital theory was implemented using multiple theoretical methods with the aim of gaining some qualitative understanding to the observations of previous experimental studies. Reaction enthalpies and barrier heights but not actual rate constants were calculated for four distinct elimination reactions of MF. Francisco concludes that the formation of methanol and CO proceeds most favorably but an additional channel, the formation of two molecules of formaldehyde, will be competitive.

Due to its intermediary role in DMM oxidation, there exists a surprising amount of literature on the hydrogen abstraction reactions thought to be most prominently involved in the atmospheric oxidation of MF. In 2000 Good and Francisco [13] investigated select reactions of the MF oxidation mechanism with *ab initio* methods. They calculate energy barriers but not the pre-exponential factors of the hydrogen abstraction reactions from MF by the OH radical, the β -scission reactions of the resultant radicals as well as for their respective addition reactions to molecular oxygen. These authors augmented this work with calculations using multiple levels of theory of the rate

constants for hydrogen abstraction from MF at both the methyl and carbonyl sites by $\dot{\text{H}}$ atom and $\dot{\text{C}}\text{H}_3$ radical [14]. These calculations conclude that hydrogen abstraction by $\dot{\text{H}}$ atom and $\dot{\text{C}}\text{H}_3$ radical from the carbonyl position occurs more readily than from the methyl position. In contrast the calculated rate constants for hydrogen abstraction by the $\dot{\text{O}}\text{H}$ radical is up to a factor-of-three times faster from the methyl position than from the carbonyl position.

In this study we characterize by experiment precise details of MF combustion over a wide range of conditions. By new estimations of the chemical reaction rate constant and thermochemical parameters involved in MF oxidation we seek to improve upon prior mechanistic work on MF oxidation.

As well as refining our understanding of the oxidation mechanism of DMM and DME, these refined parameters may be applied by analogy to larger methyl ester systems such as methyl butanoate and methyl decanoate, as put forth by Dooley [15] and Westbrook et al. [7].

2 Experimental

2.1 Shock tube

Mix	ϕ	MF	O_2	Ar	Reflected shock	Reflected shock
					pressure/atm	temperature/K
1	1.00	0.005	0.01	0.985	≈ 2.7	1285–1935
2	2.00	0.005	0.005	0.99	≈ 2.7	1275–1780
3	0.50	0.005	0.02	0.975	≈ 5.4	1420–1690
4	1.00	0.025	0.05	0.925	≈ 9.4	1310–1660

Table 1

Mixture composition mole fractions and conditions for shock tube study.

The autoignition of MF was studied at the conditions described in Table 1 using two separate shock tube facilities at NUI, Galway. The ≈ 2.7 atm data were gathered using a low pressure instrumented shock tube while the higher pressure ≈ 5.4 and ≈ 9.4 atm data were obtained with a new high pressure shock tube facility constructed at NUI, Galway. Both shock tubes were used to study MF autoignition under reflected shock conditions, the essential difference between the two instruments being the method of incident shock wave generation.

2.1.1 Low pressure shock tube

The low pressure shock tube has been described thoroughly elsewhere [16,17]. Briefly, the steel shock tube consists of a large but short (52 cm diameter and 63 cm long) driver section coupled via a 10 cm long transition piece to the test section which is 622 cm long and of 10.24 cm in internal diameter. A polycarbonate diaphragm separates the high pressure driver section from the low pressure test section. Shock waves were generated by allowing the diaphragm to burst under pressure with the assistance of a cross-shaped cutting device that petaled the diaphragm. Pressure transducers (PCB Piezotronics, model 113A21) were set into the final 50 cm of the test section and were used to measure the incident shock velocity with the aid of three universal time counters (Fluke PM6666), a fourth transducer (Kistler, 603B) is embedded in the end wall. Test gas pressures of ??-??? Torr at initial temperatures of 290–300 K were used with drive gas pressures of ??-??? Torr to generate reflected shock pressures of ≈ 2.7 atm.

2.1.2 High pressure shock tube

The high pressure shock tube facility existed in a previous incarnation in the laboratory of Prof. Cadman [18] and maintains essentially the same parameters of operation and performance. Re-commissioned in 2007, this shock tube consists of an 876 cm, stainless steel tube of internal diameter 63 mm, divided into a 300 cm long driver section and a test section 573 cm in length. The high pressure driver section is further divided for the generation of shock waves by the double diaphragm rupturing technique [19]. Polycarbonate diaphragms separate a small chamber containing helium drive gas at intermediate pressure from the high pressure drive section and the low pressure test section.

The sudden evacuation of this intermediate pressure causes both diaphragms to rupture allowing incident shock waves to form in a reproducible manner. Test gas pressures of 205–550 mbar at initial temperatures of 298–302 K were used with drive gas pressures of 10–11 atm to generate reflected shock pressures of 9.4 ± 0.4 atm. The use of drive gas pressures of 6–7 atm with test gas pressures of 70–150 Torr allowed for the generation of reflected shock pressures of 5.4 ± 0.4 atm.

Similarly to the low pressure shock tube arrangement, three pressure transducers (PCB 113A24) were set into the final 50 cm of the test section and a fourth is embedded in the end wall. In conjunction with three time counters (Fluke PM6666) these pressure sensors allow for the measurement of the incident shock velocity at three points as the shock wave passes through the test section.

2.1.3 Determination of reflected shock conditions

Reflected shock conditions (T_5 and P_5) are calculated from the measured incident shock velocity using one-dimensional shock relations [19] as implemented by the application GasEq [20]. Therefore, the repeated determination of incident shock velocity is important so as to account for any attenuation of the incident shock wave. In both shock tube facilities the extrapolation of these three measurements of the incident velocity to the end wall provides an accurate measurement of the incident shock velocity at the end wall. The estimated error [21] in the measurement of incident shock velocity corresponds to an uncertainty in reflected shock temperature of ± 7 K, such is represented by error bars in Figures 8 and 9.

2.1.4 Mixture preparation

In both shock tube apparatuses helium CP Grade 99.999%, was used as drive gas. Test gas mixtures for study in both instruments were prepared in 50 L stainless steel tanks using standard manometric methods, argon was Zero Grade 99.998%, and oxygen was Research Grade 99.985%. All gases were obtained from BOC Ireland Ltd and used without further purification. MF as 99.5% pure was obtained from Aldrich Chemical Co. Ltd. To minimize the presence of atmospheric air in the liquid fuel the sample was subjected to several freeze-pump-thaw degassing cycles before being incorporated into the test mixture by vaporization into the evacuated mixing tanks. As low test gas pressures were required for study in the low pressure shock tube, this mixing tank and test section were evacuated to 10^{-6} Torr to eliminate any potential contaminants. The higher pressure experiments required a much higher test gas pressure and therefore are not as sensitive to contamination, this mixing tank and test section were evacuated to 10^{-2} Torr before mixture preparation.

In the case of the low pressure shock tube, partial pressures of fuel and oxygen were measured using a 100 Torr Baratron gauge to an accuracy of 0.01 Torr. Argon was added using an 900 Torr digital manometer (Chell cd101). The high pressure shock tube facility uses a Wallace and Tiernan (61b-1a-0050e) 0–3400 mbar pressure gauge to measure fuel, oxygen and diluent partial pressures. In both apparatuses test gas mixtures were normally made up to a final pressure of 800 Torr and allowed to stand for at least 12 hours to ensure homogeneity.

2.1.5 Ignition delay time

In the low pressure shock tube light emission was observed using an end-on detection diagnostic that consisted of a PDA55 (switchable gain, amplified silicon detector). A photomultiplier tube was used with the high pressure facility. Each were aligned behind a 431.5 nm (CH^* emission) narrow bandpass

filter with a spectral bandwidth of 10 nm. The filters and the light diagnostic were aligned behind quartz windows located in each end wall. The pressure transducers, mounted flush with each end wall, signaled the shock wave arrival at the end wall and the beginning of the ignition delay period. The end of the period was defined as the maximum rise in the rate of CH^* emission.

2.2 Variable pressure flow reactor

The design and operating characteristics of the Princeton Variable Pressure Flow Reactor (VPFR) have been discussed in detail elsewhere [22]. In the present experiments, nitrogen carrier gas was heated by an electric resistance heater and mixed with oxygen as it entered a 10.2 cm diameter quartz test section. MF (99.5%, Aldrich Chemical Co. Ltd.) was supplied from a liquid evaporator system, diluted with additional nitrogen. The diluted fuel vapor was rapidly mixed with the oxygen and carrier gases at the entrance to a conical shaped silica foam diffuser.

The reacting mixture was sampled at axial positions downstream of the diffuser using a hot-water-cooled, stainless steel sampling probe, which continuously extracts and convectively quenches a small percentage of the flow. Moving the location of the mixer-diffuser within the test section varied the distance from the diffuser to the fixed location of the sampling probe. The reaction temperature of flow at the sampling location, with all flows established except the fuel flow, varied by less than ± 2 K, independent of the location of the mixer diffuser in the test section.

During operation of the VPFR, all flow rates of carrier, diluent, and reactants were metered and held constant for the entire duration of each set of experiments reported. The initial reaction temperature not accounting for combus-tive heat release was held constant. Throughout the course of each experiment the reaction pressure was modified so as to maintain the initial pressure. The reaction temperature at the sampling location and all sample analytical readings were allowed to achieve steady state, before the data were digitally recorded.

2.3 Residence time

The reaction time for a specific location of the diffuser was calculated using experimental axial velocity profile information downstream of the diffuser, determined under cold flow conditions, and corrected for reaction conditions using a Reynolds number correlation technique. The residence time of the reactants inside the VPFR was altered by moving the location of the mixer

diffuser. This procedure was employed at discrete intervals of diffuser position to obtain a new set of composition data and sample temperature for the new reaction time. The resulting data were then assembled to produce the species histories reported for a given set of initial mixture condition, initial temperature, and reaction pressure.

2.4 Sample analysis

The sampled gas flow was transferred through heated Teflon lines to a series of analytical equipment including a Fourier transform infrared (FTIR) spectrometer (Nicolet Model 560), an electrochemical oxygen (O_2) analyzer (Infrared Industries Model 2200), and non-dispersive carbon monoxide (CO) and carbon dioxide (CO_2) analyzers (Horiba Model PIR 2000). The uncertainties in the measurements reported here are: $\text{O}_2 \leq 4\%$; $\text{CO} \leq 3\%$; $\text{CO}_2 \leq 3\%$ of the reading. The other major species identified during the oxidation of MF were H_2O (water), CH_3OH (methanol), CH_2O (formaldehyde) and CH_4 (methane). The FTIR was calibrated to measure the concentration of these species as well as MF by recording the FTIR spectra for known mole fractions of these species in nitrogen. The calibrations use the FTIR response signal at wavelengths where only the species in question was the major absorber. Estimated uncertainties in the measurements of these species are: $\text{H}_2\text{O} \leq 5\%$; $\text{MF} \leq 3\%$; $\text{CH}_3\text{OH} \leq 3\%$; $\text{CH}_2\text{O} \leq 10\%$ and $\text{CH}_4 \leq 3\%$ of the reported value. All scanned FTIR wavelengths were digitally recorded, thus allowing reprocessing of all acquired data for identifying any reaction species not originally characterized.

2.5 Conditions of study

Set	ϕ	MF	O_2	N_2	T/K
1	0.5	0.005	0.02	0.975	900
2	1.0	0.005	0.01	0.985	903
3	1.5	0.005	0.0067	0.988	900

Table 2

Mixture composition mole fractions for 3 atm flow reactor study.

The oxidation of MF was studied using 0.5% fuel, at three equivalence ratios; 0.5, 1.0 and 1.5. Pressure and temperature were held constant at 3 atm and near 900 K, Table 2. The reaction was followed as a function of time until the fuel and major intermediates had been consumed, ≈ 0.7 seconds.

2.6 Dual chambered cylindrical bomb

Fig. 1. Schlieren images of MF/synthetic air flames of approximately 3 cm radius; (A) $\phi = 0.8$, (B) $\phi = 1.0$ and (C) $\phi = 1.6$.

The burning velocities of MF/O₂/N₂ flames were measured as a function of equivalence ratio using outwardly propagating flames in a dual-chambered, pressure-release type high-pressure combustion apparatus as described in detail elsewhere [23]. In the present study, the device was operated in the “closed” configuration, and may be treated as a constant-volume cylindrical bomb. Mixtures were prepared in the constant volume chamber by the partial pressure method using an absolute pressure gauge (Cecomp Electronics Inc.) accurate to ± 1.5 mbar. For all experiments MF (anhydrous, 99%, Aldrich Chemical Co. Ltd.) was diluted to a pressure of 1 atm with synthetic air, i.e. O₂:N₂ = 1:3.78, consisting of Zero Grade nitrogen (99.998%) and Research Grade oxygen (99.5%) supplied by Airgas Ltd. Due care was taken to ensure that there was minimal contamination of the MF vapor in filling the combustion chamber. The mixtures were allowed to homogenise for at least 30 minutes prior to spark induced ignition by a high voltage tungsten filament. The initial temperature of each experiment was 295 ± 2 K.

High-speed Schlieren photography was used to observe the flame propagation. Figure 1 shows the flame surface structure for representative equivalence ratios of 0.8, 1.0, and 1.6 at a flame radius of ≈ 3 cm. For fuel-lean conditions, the flame surface is completely smooth. For richer mixtures, cracks on the flame surface resulting from the ignition event were retained throughout flame propagation, Figure 1(c). However, for all conditions, new cells did not appear during the observed period of propagation i.e. for flame radii up to 3 cm after an early period influenced by the electrodes. The lack of formation of new cells that would induce flame acceleration indicates that the linear relationship between stretch rate and flame speed is applicable [24]. Our experimental observations (such as those presented in Figure 2) are consistent with this statement. The instantaneous flame speed (s_u) is calculated using the flow correction term (ϖ) of Burke et al. [25]. The flow correction term is employed to account for the actual gas motions induced by combustion in a cylindrical chamber, rather than the conventional zero burned gas velocity assumption ($\varpi = 0$) which is valid for a non-confined system. The expansion factor (σ) is defined as the ratio of the unburned to burned gas densities across the flame

Fig. 2. The determination of the laminar burning velocity for MF/synthetic air flames, experiment (symbols) and extrapolation to s_u^o (lines); $\triangle$ — $\phi = 0.8$, $\square$ — $\phi = 1.6$ and $\bullet$ — $\phi = 1.0$.

front, Equation 1.

$$s_u = \frac{\frac{1}{\sigma} \frac{dr_f}{dt}}{(1 + \frac{\sigma-1}{\sigma} \varpi)} \quad (1)$$

The definition of stretch rate (κ) is that of Strehlow and Savage [26] and may be related to the flame radius (r_f) and flame front velocity ($\frac{dr_f}{dt}$) by;

$$\kappa = \frac{2}{r_f} \frac{dr_f}{dt} \quad (2)$$

The laminar burning velocity (s_u^o), is obtained through linear extrapolation of the flame speed to a value of zero stretch rate using a linear stretch relation,

$$s_u = s_u^o - \kappa L_u \quad (3)$$

where L_u is the Markstein length [27].

The flow-corrected flame speed is shown as a function of flame stretch rate in Figure 2 for the three equivalence ratios captured in Figure 1. Unsteady ignition effects, as described by Chen et al. [28], were observed for small flame radii up to flame radii of 1 cm for some equivalence ratios. To test

the influence of these effects and the reproducibility of measurement, four experiments were performed for the stoichiometric condition where the mixing time was also varied between 30 and 120 minutes. The flame speed *verses* stretch trajectories vary from experiment to experiment for small flame radii (large stretch rates) which is indicative of unsteady flame behavior dependent on ignition energy. Importantly the four cases converge onto the quasi-steady branch for larger flame radii (smaller stretch rates), Figure 2. The flame speed is observed to depend linearly on stretch rate for flames larger than 1 cm in radius. Therefore, linear extrapolation to the laminar burning velocity is performed for flame radii ranging from 1 to 2 cm where the quasi-steady linear stretch relationship appears to be applicable. This methodology was tested by extrapolating to zero stretch rate over four distinct ranges of flame radii (from 1 to 3 cm) for each experiment. This treatment produced burning velocities which were typically consistent within 3% (the value of the error bars presented in Figure 13, page 35). All other values presented are obtained from single experiments.

The experimental data for all measurements reported in this study are presented as supplementary materials.

3 Kinetic model

A detailed chemical kinetic model for MF oxidation has been developed and used to simulate the experimental data herein. In this section we describe the construction of the kinetic model with particular attention to the MF submechanism, the chemical reactions and Arrhenius parameters of which are listed in Tables 4–6.

3.1 Base mechanism

As the molecular structure of MF is void of C—C bonds we expect the formation of any C₂ species during MF oxidation to be minimal, indeed no C₂ intermediate species were observed in the flow reactor experiments. However they may be formed from bimolecular abstraction and recombination reactions and we include these reactions in our submechanism which is composed of the C₁ chemistry of Zhao et al. [29, 30] up to and inclusive of the reaction $\dot{\text{C}}\text{H}_3 + \dot{\text{C}}\text{H}_3 (+\text{M}) \rightleftharpoons \text{C}_2\text{H}_6 (+\text{M})$. The ethane consumption chemistry is described by a C₂ and C₃ submechanism which was recently validated by Healy et al. [31]. This particular set of base chemistry was chosen for its accuracy in describing the oxidation of methanol, a primary intermediate species in MF oxidation. Also included, based on the submechanisms of Westbrook et al. [7]

is chemistry to describe the consumption of the larger esters, methyl acetate and ethyl formate.

3.2 Methyl formate chemistry

3.2.1 Thermochemistry

Hall and Baldt have measured by bomb calorimetry H_{f298K}^o of MF as -84.97 kcal mol⁻¹ [32]. There are a number of non-experimental studies in the literature which describe the influence of the ester functionality on any surrounding atoms and bonds; Good and Francisco [13], Glaude *et al.* [33] and Sumanthi and Green [34] have all computed H_{f298K}^o for MF as well as several species formed by its decomposition. The C—H bond dissociation enthalpies (BDE) which result from these works are shown in Table 3.

Bond	Good & Francisco [13]	Glaude et al. [33]	Sumanthi & Green [34]
CH ₃ OCO—H	100.3	100.3	100.1
H—CH ₂ OCHO	101.3	101.9	100.9
MF H_{f298K}^o	-85.7	- 86.0	-85.9

Table 3

MF bond dissociation energies and H_{f298K}^o . Reference data; $\dot{H}$ atom $H_{f298K}^o = 52.1$ kcal mol⁻¹ [35]. All units are kcal mol⁻¹.

We have chosen to generate the thermochemical input for the kinetic model with use of the group values recommended by Sumanthi & Green [34]. We implement these values by the method of group additivity [36] as implemented through *THERM* [37], and arrive at a set of BDEs as shown in Figure 3. The thermochemical parameters of oxygenated species are not as well known as those of conventional hydrocarbon fuels, nevertheless this data is of primary importance in the construction of chemical kinetic models, particularly in the treatment of the important hydrogen abstraction reactions. Moreover oxygenated fuels can exhibit unorthodox C—H BDEs, particularly if these bonds are in close proximity to the electronegative oxygen atoms. As most of the available rate constant data deals with conventional hydrocarbon fuels, this facet of the detailed modeling of oxygenates represents a significant challenge.

Fig. 3. Methyl formate bond enthalpies at 298 K / kcal mol⁻¹.

3.2.2 Hydrogen abstraction from fuel

It is our intention to develop a deductive/*a priori* approach to the estimation of the rate of hydrogen abstraction from systems of such unorthodox C—H BDEs. We assume that the rate of abstraction is dependent on the identity of the abstracting radical and on the strength of the C—H bond. Hydrogen abstraction from MF may occur from two locations producing the radical species $\text{CH}_3\dot{\text{O}}\text{CO}$ and $\dot{\text{C}}\text{H}_2\text{OCHO}$. From Table 3 all values for the $\text{CH}_3\text{OCO—H}$ BDE are in excellent agreement, but the reported values for the $\text{H—CH}_2\text{OCHO}$ BDE differ by $\approx 1 \text{ kcal mol}^{-1}$. Therefore our treatment of hydrogen abstraction from this site is a source of error in the kinetic model. We use the extensively reviewed literature data [40–48] on hydrogen abstraction from regular hydrocarbons (such as propane and ethane) to correlate the rate constant of hydrogen abstraction with the BDE on a per $\dot{\text{H}}$ atom basis for C—H BDEs of 100.1 and 100.9 kcal mol^{-1} respectively. This method allows the sensitivity to the rate of hydrogen abstraction to be confidently tested within the known uncertainties of the thermochemical parameters.

Hydrogen abstraction by eleven small radical species common to any combusting system is considered as well as by the fuel alkyl radicals $\text{CH}_3\dot{\text{O}}\text{CO}$ and $\dot{\text{C}}\text{H}_2\text{OCHO}$ and by the $\dot{\text{O}}\text{CHO}$ radical which is a product of MF decomposition. Typically our estimated rate constants for hydrogen abstraction from the $\text{H—CH}_2\text{OCHO}$ position are 95% of the values for a typical primary C—H bond (as in propane). The weaker bond strength of the $\text{CH}_3\text{OCO—H}$ position means that our estimated rate constants for abstraction from this position are of intermediate values between typical primary and secondary C—H bonds. For example, at 1500 K hydrogen abstraction by $\dot{\text{H}}$ atom and $\text{H}\dot{\text{O}}_2$ radical are respectively 77% and 79% of the values recommended by Orme et al. [40] for hydrogen abstraction from a typical primary C—H bond.

In comparison to the calculations of Good and Francisco [13], we may make no consistent remark regarding the qualitative agreement of each set of calculated rate constants. Regarding hydrogen abstraction by $\dot{\text{H}}$ atom, at 1500K, our estimate is 3.6 and 1.35 times faster than the calculations of Good and Francisco for abstraction from the $\text{H—CH}_2\text{OCHO}$ and $\text{CH}_3\text{OCO—H}$ positions respectively. For abstraction by $\dot{\text{C}}\text{H}_3$ radical at 1500 K our estimate is 1.29 times faster for abstraction from the $\text{H—CH}_2\text{OCHO}$ position, but a much larger 12.58 times slower from the $\text{CH}_3\text{OCO—H}$ position. Finally our estimates for hydrogen abstraction by $\dot{\text{O}}\text{H}$ radical at 1500K are 0.98 and 0.86 times the rate constants of Good and Francisco for abstraction from the $\text{H—CH}_2\text{OCHO}$ and $\text{CH}_3\text{OCO—H}$ sites respectively.

3.2.3 Fuel decomposition

It has been assumed that the C=O bond of the ester functionality remains intact during the global MF oxidation reaction i.e. no chemistry is considered from this centre and MF may only homolytically decompose by fission of C—H and C—O bonds. The high-pressure limit rate expressions for these reactions have been estimated in the reverse recombination direction which is taken to be a barrierless process. The forward decomposition expression is computed from microscopic reversibility and in this manner the BDE is taken into account. MF may also decompose through a number of concerted molecular elimination reactions. We consider two channels; $\text{MF} \rightleftharpoons \text{CH}_3\text{OH} + \text{CO}$ and $\text{MF} \rightleftharpoons \text{CH}_4 + \text{CO}_2$.

Francisco [12] has calculated the energy barrier for the reaction forming $\text{CH}_3\text{OH} + \text{CO}$ at six levels of theory to be 74–77 kcal mol^{−1}. However reported experimental values for this energy barrier span a lower range of 48.7–50.6 kcal mol^{−1} [8–10]. Consequently the overall rate constant of this three-centered reaction is not known. In this study it has been taken to equal that of the four-centered unimolecular elimination reaction of methyl tert-butyl ether (MTBE) forming isobutene and methanol:

This reaction has been studied by experiment four times and a NIST kinetic database [49] fit yields a rate expression of $1.00 \times 10^{14} \exp(-60,000 \text{ cal mol}^{-1}/RT)$ cm³ mol^{−1} s^{−1}. This analogy seems reasonable as the ring strain values for three and four membered ring transition states are recommended by Benson [36] to be 26.9 and 25.7 kcal mol^{−1} respectively. In addition, the frequency factors for these reactions ought to be similar. The MF transition state ties up one less rotor than that for MTBE, and so should be almost an order of magnitude faster. However, MTBE has nine hydrogen atoms available for the transition state, compared to only one in the case of MF, and so the frequency factors should be very similar.

Recognizing that the branching ratio between MF decomposing to $\text{CH}_3\text{OH} + \text{CO}$ and to $\text{CH}_4 + \text{CO}_2$ will likely be as important as the absolute value of the rate constants, we have estimated our rate expression for the latter channel

from our estimate of the former. In this regard the transition state leading to $\text{CH}_4 + \text{CO}_2$ is four centered and therefore eliminates one more rotor than the three-centred reaction. This ought to lower the frequency factor by almost an order of magnitude, while the activation energy should be only slightly lower. We estimate a rate expression for the reaction $\text{MF} \rightleftharpoons \text{CH}_4 + \text{CO}_2$ of $8.00 \times 10^{12} \exp(-59,000 \text{ cal mol}^{-1}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Again in this instance we apparently disagree with the calculations of Francisco [12], who has computed the barrier to formation of $\text{CH}_4 + \text{CO}_2$ to be higher than that for $\text{CH}_3\text{OH} + \text{CO}$ formation, lying at $\approx 85 \text{ kcal mol}^{-1}$. Glaude et al. observed a similar discrepancy when studying the elimination of dimethyl carbonate to dimethyl ether and carbon dioxide. They calculate the barrier to this four-centred reaction with the CBS-Q method to be $\approx 70 \text{ kcal mol}^{-1}$, ten kcal mol^{-1} higher than for a typical four centered elimination. We evaluate the rate constants for these processes generated from the calculations of Francisco against experimental data later. The rate constants for the reactions, $\text{MF} \rightleftharpoons \text{CH}_3\text{OH} + \text{CO}$, $\text{MF} \rightleftharpoons \text{CH}_4 + \text{CO}_2$ and $\text{MF} \rightleftharpoons \dot{\text{C}}\text{H}_3 + \dot{\text{O}}\text{CHO}$ have also been treated using quantum Rice-Ramsperger-Kassel theory with a master equation analysis [50] in order to account for pressure fall-off.

Alkyl radical decomposition

Hydrogen abstraction from MF can produce two alkyl radicals, $\text{CH}_3\text{O}\dot{\text{C}}\text{O}$ and $\dot{\text{C}}\text{H}_2\text{OCHO}$. The kinetics of the $\text{CH}_3\text{O}\dot{\text{C}}\text{O}$ (methoxy formyl) radical decomposition is one of many mechanisms which may lead to CO_2 production from biodiesel and other oxygenates containing the ester functional group. For this reason its decomposition has received much attention. In 2000, with G2 and G2(MP2) methods Good & Francisco [13] calculated the activation energies of $14.7 \text{ kcal mol}^{-1}$ for $\text{CH}_3\text{O}\dot{\text{C}}\text{O} \rightleftharpoons \dot{\text{C}}\text{H}_3 + \text{CO}_2$ and $21.9 \text{ kcal mol}^{-1}$ for $\text{CH}_3\text{O}\dot{\text{C}}\text{O} \rightleftharpoons \text{CH}_3\dot{\text{O}} + \text{CO}$ respectively. This work agrees with the work of McCunn et al. [38] and in particular with the work of Glaude et al. [33] who calculated barriers of $14.7 \text{ kcal mol}^{-1}$ to $\dot{\text{C}}\text{H}_3 + \text{CO}_2$ and $22.7 \text{ kcal mol}^{-1}$ to $\text{CH}_3\dot{\text{O}} + \text{CO}$. These authors also determine actual rate constants of $4.76 \times 10^7 T^{1.54} \exp(-34,700 \text{ cal mol}^{-1}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for $\dot{\text{C}}\text{H}_3 + \text{CO}_2 \rightleftharpoons \text{CH}_3\text{O}\dot{\text{C}}\text{O}$ and $1.55 \times 10^6 T^{-2.02} \exp(-5,730 \text{ cal mol}^{-1}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for $\text{CH}_3\dot{\text{O}} + \text{CO} \rightleftharpoons \text{CH}_3\text{O}\dot{\text{C}}\text{O}$ respectively.

Very recently, Huynh and Violi [39] also analysed this branching ratio using a G3//B3LYP-B3LYP/6-31G(d) composite method. They have calculated both forward and reverse rate constants for each channel. Their rate constant for $\dot{\text{C}}\text{H}_3 + \text{CO}_2 \rightleftharpoons \text{CH}_3\text{O}\dot{\text{C}}\text{O}$ is more than an order of magnitude slower than the expression of Glaude et al [33]. While the expression reported by these authors for $\text{CH}_3\dot{\text{O}} + \text{CO} \rightleftharpoons \text{CH}_3\text{O}\dot{\text{C}}\text{O}$ is in much better agreement with that of Glaude et al., only approximately a factor-of-two slower. In order to test our thermochemical parameters so that they may be confidently extended to

other systems we allow all reactions to be in thermodynamic equilibrium by defining each reaction in one direction only. The modeling simulations of the laminar burning velocities presented in *this study* are quite sensitive to the decomposition of the methoxy formyl radical and so we have chosen to use the expressions of Glaude et al. as they result in better agreement, though only slightly so than with use of those of Huynh and Violi.

By contrast, the decomposition of the $\dot{\text{C}}\text{H}_2\text{OCHO}$ radical is not as well known as that of the $\text{CH}_3\text{O}\dot{\text{C}}\text{O}$ radical. The sum of the available literature data on this reaction equates to an activation energy value of $30.8 \text{ kcal mol}^{-1}$ computed as above by Good and Francisco [13]. As per our treatment of fission reactions the rate constant of this reaction has been estimated in the reverse addition direction [51]. Our original treatment for this reaction was to adopt the values used by Dooley et al. [15] to describe the analogous process in methyl butanoate oxidation which likens the n-propylformyl radical to the vinyl radical:

Based on quantum chemical calculations for the addition reactions of the vinyl radical to various compounds they opted for an expression of $3.89 \times 10^{11} \exp(-10,900 \text{ cal mol}^{-1}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ to describe this analogous process for methyl butanoate. The kinetic model for MF oxidation presented here can not reproduce the laminar burning velocities if this rate constant is used for the reaction $\text{H}\dot{\text{C}}\text{O} + \text{CH}_2\text{O} \rightleftharpoons \dot{\text{C}}\text{H}_2\text{OCHO}$ with the result that although the effect of equivalence ratio is well described the laminar burning velocity is too fast over all conditions by $\approx 20\%$. This non extendability represents a lack of understanding of the β -scission processes of ester radicals and their competition with inter radical isomerisation reactions. We have decided to fix the $\text{CH}_3\text{O}\dot{\text{C}}\text{O} \rightleftharpoons \dot{\text{C}}\text{H}_2\text{OCHO}$ isomerisation rate constant at $2.62 \times 10^{11} T^{-0.03} \exp(-38,178 \text{ cal mol}^{-1}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which is the value recommended by Fisher et al. [6] in their kinetic model for MF oxidation. Thus a value of $3.89 \times 10^{11} \exp(-23,000 \text{ cal mol}^{-1}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which comprises the pre-exponential factor of Dooley et al. above and a value for the activation energy which is more akin to that recommended by Rauk et al. [52] for methyl radical addition to formaldehyde than vinyl radical addition has been used for the reaction $\text{H}\dot{\text{C}}\text{O} + \text{CH}_2\text{O} \rightleftharpoons \dot{\text{C}}\text{H}_2\text{OCHO}$.

Low temperature oxidation pathway

Although no low temperature (≤ 900 K) data has been reported for MF oxidation the present model allows the alkyl radicals formed by hydrogen abstraction to undergo addition to molecular oxygen to form the $\text{R}\dot{\text{O}}_2$ species which have been shown to lead to the oxidation of other fuels at low temperature, for example see the works of Zhao et al. [30] and Curran et al. [53].

This low temperature pathway has been adopted and modified from the work of Fisher et al. [6] but its exertions remain ostensibly unvalidated by this (or any other) study. We have made two more significant and a number of relatively minor modifications from the adopted pathway of Fisher et al.; the thermochemistry of species involved in the low temperature MF submechanism have been re-estimated so as to be consistent with those of the high temperature MF mechanism i.e. we incorporate the work of Sumanthi and Green [34].

Though not for MF, Hayes and Burgees [54] have recently computed rate constants and activation energy barriers for a number of $\text{R}\dot{\text{O}}_2 \rightleftharpoons \dot{\text{Q}}\text{O}_2\text{H}$ isomerisation reactions for larger n -alkyl methyl esters. They have found that those $\text{R}\dot{\text{O}}_2$ species where the radical center is in proximity to the ester moiety exhibit larger activation energies to internal hydrogen atom abstraction in comparison to the equivalent (in terms of the number of atoms involved in the transition state) reactions of the $\text{R}\dot{\text{O}}_2$ species of n -alkanes. Specifically these authors have shown for methyl butanoate, the activation energy barrier to the seven-centered isomerisation transition geometry of the $\text{R}\dot{\text{O}}_2$ species which forms at the methyl position is 6 kcal mol^{-1} higher than the equivalent isomerisation in n -heptane [53]. Therefore in this study, the rate constants which describe the $\text{R}\dot{\text{O}}_2 \rightleftharpoons \dot{\text{Q}}\text{O}_2\text{H}$ isomerisation reactions for both fuel alkylperoxy radicals ($\text{R}\dot{\text{O}}_2$) have been estimated from the work of Curran et al. [53] but the activation energy barriers for each channel have been increased by 6 kcal mol^{-1} , consistent in an approximate manner with the recent work of Hayes and Burgees et al. [54]. Significantly, if the model is exercised under appropriate conditions this updated low temperature pathway predicts low temperature reactivity and negative temperature coefficient behavior for MF oxidation.

3.3 Transport parameters

In order to simulate the burning velocity data transport parameters for species of the MF sub mechanism have been estimated based on species of similar molecular mass from the dimethyl ether kinetic mechanism of Zhao et al. [30].

Reaction	$A/cm^3 mol^{-1} s^{-1}$	n	$E_A/cal mol^{-1}$	Reference
$CH_3OCHO \leftrightarrow CH_3OH + CO$	1.00E + 14	0.0	60000.0	†
low pressure limit	1.11E+62	-11.71	71104	
$T^A=0.003$	$T^{***}=2.34E+02$	$T^*=8.33E+09$	$T^{**}=3.28E+09$	
$CH_3OCHO \leftrightarrow CH_4 + CO_2$	8.00E + 12	0.0	59000.0	†
low pressure limit	4.70E+62	-13.0	70910	
$T^A=0.8681$	$T^{***}=9.86E+09$	$T^*=2.91$	$T^{**}=3.28E+09$	
$CH_3OCHO \leftrightarrow \dot{C}H_3 + \dot{O}CHO$	2.17E+24	-2.40	92600.0	†
low pressure limit	5.71E+47	-84.3	98490.0	
$T^A=6.89E-15$	$T^{***}=4.73E+03$	$T^*=9.33E+09$	$T^{**}=1.78E+09$	

Table 4

Arrhenius and Troe fall-off parameters for reactions of the methyl formate submechanism; High temperature, pressure dependent. † *this study*.

Reaction	$A/cm^3 mol^{-1} s^{-1}$	n	$E_A/cal mol^{-1}$	Reference
$\dot{H} + \dot{C}H_2OCHO \rightleftharpoons CH_3OCHO$	1.00E + 14	0.0	0.0	$\dot{R} + \dot{H}$ [53]
$\dot{H} + CH_3O\dot{C}O \rightleftharpoons CH_3OCHO$	1.00E + 14	0.0	0.0	$\dot{R} + \dot{H}$ [53]
$CH_3\dot{O} + H\dot{C}O \rightleftharpoons CH_3OCHO$	3.00E + 13	0.0	0.0	$\dot{C}H_3 + \dot{R}$ [53]
$CH_3OCHO + \dot{H} \rightleftharpoons \dot{C}H_2OCHO + H_2$	6.65E + 05	2.5	6494.2	†
$CH_3OCHO + \dot{O}H \rightleftharpoons \dot{C}H_2OCHO + H_2O$	8.86E + 12	0.1	3340.5	†
$CH_3OCHO + \dot{C}H_3 \rightleftharpoons \dot{C}H_2OCHO + CH_4$	2.91E - 01	3.7	6823.8	†
$CH_3OCHO + H\dot{O}_2 \rightleftharpoons \dot{C}H_2OCHO + H_2O_2$	5.66E + 04	2.4	16594.3	†
$CH_3OCHO + CH_3\dot{O}_2 \rightleftharpoons \dot{C}H_2OCHO + CH_3O_2H$	5.66E + 04	2.4	16594.3	†
$CH_3OCHO + CH_3\dot{O} \rightleftharpoons \dot{C}H_2OCHO + CH_3OH$	4.59E + 09	0.5	4823.6	†
$CH_3OCHO + \ddot{O} \rightleftharpoons \dot{C}H_2OCHO + \dot{O}H$	8.84E + 05	2.4	4593.2	†
$CH_3OCHO + O_2 \rightleftharpoons \dot{C}H_2OCHO + H\dot{O}_2$	1.53E + 13	0.1	51749.8	†
$CH_3OCHO + H\dot{C}O \rightleftharpoons \dot{C}H_2OCHO + CH_2O$	1.02E + 05	2.5	18430.0	†
$CH_3OCHO + \dot{O}CHO \rightleftharpoons \dot{C}H_2OCHO + HCOOH$	5.66E + 04	2.4	16594.3	† as $H\dot{O}_2$
$CH_3OCHO + \dot{H} \rightleftharpoons CH_3O\dot{C}O + H_2$	2.58E + 05	2.5	5736.8	†
$CH_3OCHO + \dot{O}H \rightleftharpoons CH_3O\dot{C}O + H_2O$	1.22E + 16	-1.0	4946.1	†
$CH_3OCHO + \dot{C}H_3 \rightleftharpoons CH_3O\dot{C}O + CH_4$	9.21E - 02	3.7	6052.6	†
$CH_3OCHO + H\dot{O}_2 \rightleftharpoons CH_3O\dot{C}O + H_2O_2$	1.57E + 05	2.2	16544.4	†
$CH_3OCHO + CH_3\dot{O}_2 \rightleftharpoons CH_3O\dot{C}O + CH_3O_2H$	1.57E + 05	2.2	16544.4	†
$CH_3OCHO + CH_3\dot{O} \rightleftharpoons CH_3O\dot{C}O + CH_3OH$	5.27E + 09	0.8	2912.4	†
$CH_3OCHO + \ddot{O} \rightleftharpoons CH_3O\dot{C}O + \dot{O}H$	2.45E + 05	2.5	4047.8	†
$CH_3OCHO + O_2 \rightleftharpoons CH_3O\dot{C}O + H\dot{O}_2$	3.85E + 12	0.1	50759.6	†
$CH_3OCHO + \dot{O}CHO \rightleftharpoons CH_3O\dot{C}O + HCOOH$	1.57E + 05	2.2	16544.4	† as $H\dot{O}_2$
$CH_3OCHO + H\dot{C}O \rightleftharpoons CH_3O\dot{C}O + CH_2O$	5.40E + 06	1.9	17010.0	† as $H\dot{O}_2$
$\dot{C}H_3 + CO_2 \rightleftharpoons CH_3O\dot{C}O$	4.76E + 07	1.5	34700.0	[33]
$CH_3\dot{O} + CO \rightleftharpoons CH_3O\dot{C}O$	1.55E + 06	2.0	5730.0	[33]
$\dot{C}H_2OCHO \rightleftharpoons CH_3O\dot{C}O$	2.62E + 11	0.0	38178.0	[6]
$CH_2O + H\dot{C}O \rightleftharpoons \dot{C}H_2OCHO$	3.89E + 11	0.0	22000.0	†
$CH_3O\dot{C}O + CH_3OCHO \rightleftharpoons CH_3OCHO + \dot{C}H_2OCHO$	3.00E + 11	0.0	10400.0	†
$\dot{C}H_3 + \dot{C}H_2OCHO \rightleftharpoons CH_3CH_2OCHO$	3.00E + 13	0.0	0.0	$\dot{C}H_3 + \dot{R}$ [53]
$\dot{C}H_3 + CH_3O\dot{C}O \rightleftharpoons CH_3CO_2CH_3$	3.00E + 13	0.0	0.0	$\dot{C}H_3 + \dot{R}$ [53]

Table 5

Arrhenius parameters for reactions of the methyl formate submechanism; High temperature, † *this study*.

Reaction	$A/cm^3 mol^{-1} s^{-1}$	n	$E_A/cal mol^{-1}$	Reference
$\dot{C}H_2OCHO + \dot{H}O_2 \rightleftharpoons \dot{O}CH_2OCHO + \dot{O}H$	7.00E + 12	0.0	-1000.0	$\dot{C}H_3 + \dot{H}\dot{O}_2$ [46]
$CH_3\dot{O}\dot{C}O + \dot{H}O_2 \rightleftharpoons CH_3OC * \dot{O}\dot{O} + \dot{O}H$	7.00E + 12	0.0	-1000.0	$\dot{C}H_3 + \dot{H}\dot{O}_2$ [46]
$\dot{C}H_2OCHO + CH_3\dot{O} \rightleftharpoons \dot{O}CH_2OCHO + \dot{C}H_3$	7.00E + 12	0.0	-1000.0	$\dot{C}H_3 + \dot{H}\dot{O}_2$ [46]
$CH_3\dot{O}\dot{C}O + CH_3\dot{O} \rightleftharpoons CH_3OC * \dot{O}\dot{O} + \dot{C}H_3$	7.00E + 12	0.0	-1000.0	$\dot{C}H_3 + \dot{H}\dot{O}_2$ [46]
$CO_2 + CH_3\dot{O} \rightleftharpoons \dot{O}CH_2OCHO$	1.00E + 11	0.0	9200.0	[6]
$CH_2O + \dot{O}CHO \rightleftharpoons CH_3OC * \dot{O}\dot{O}$	3.89E + 11	0.0	2500.0	$\dot{C}_2H_3 + CH_2O$ [52]
$CH_3\dot{O}\dot{C}O + O_2 \rightleftharpoons CH_3OC * \dot{O}\dot{O}\dot{O}$	4.52E + 12	0.0	0.0	$nC_7\ 1^\circ + O_2$ [53]
$\dot{C}H_2OCHO + O_2 \rightleftharpoons \dot{O}OCH_2OCHO$	4.52E + 12	0.0	0.0	$nC_7\ 1^\circ + O_2$ [53]
$\dot{O}OCH_2OCHO \rightleftharpoons HOOCH_2\dot{O}\dot{C} * O$	2.47E + 11	0.0	28900.0	†
$CH_3OC * \dot{O}\dot{O}\dot{O} \rightleftharpoons \dot{C}H_2OC * \dot{O}\dot{O}\dot{O}H$	7.41E + 11	0.0	28900.0	†
$\dot{C}H_2O_2H + CO_2 \rightleftharpoons HOOCH_2\dot{O}\dot{C} * O$	2.92E + 06	1.6	36591.0	$\dot{C}H_3 + CO_2$ [39]
$\dot{O}CH_2O_2H + CO \rightleftharpoons HOOCH_2\dot{O}\dot{C} * O$	1.08E + 07	1.6	5588.0	$CH_3\dot{O} + CO$ [39]
$\dot{O}H + CH_2O \rightleftharpoons \dot{C}H_2O_2H$	2.30E + 10	0.0	12900.0	†
$\dot{O}CH_2O_2H \rightleftharpoons CH_2O + \dot{H}\dot{O}_2$	1.27E + 18	-1.8	10460.0	[55]
$\dot{C}H_2OC * \dot{O}\dot{O}\dot{O}H \rightleftharpoons CH_2O + CO_2 + \dot{O}H$	3.80E + 18	-1.5	37360.0	[6]
$\dot{C}H_2OC * \dot{O}\dot{O}\dot{O}H \rightleftharpoons CH_2O + CO + \dot{H}\dot{O}_2$	3.80E + 18	-1.5	37360.0	[6]
$\dot{C}H_2OC * \dot{O}\dot{O}\dot{O}H \rightleftharpoons cyOCH_2OC * O + \dot{O}H$	7.50E + 10	0.0	15250.0	[6]
$HOOCH_2\dot{O}\dot{C} * O \rightleftharpoons cyOCH_2OC * O + \dot{O}H$	7.50E + 10	0.0	15250.0	[6]
$\dot{C}H_2OC * \dot{O}\dot{O}\dot{O}H + O_2 \rightleftharpoons \dot{O}OCH_2OC * \dot{O}\dot{O}\dot{O}H$	4.52E + 12	0.0	0.0	$nC_7\ 1^\circ + O_2$ [53]
$HOOCH_2\dot{O}\dot{C} * O + O_2 \rightleftharpoons HOOCH_2OC * \dot{O}\dot{O}\dot{O}$	4.52E + 12	0.0	0.0	$nC_7\ 1^\circ + O_2$ [53]
$\dot{O}OCH_2OC * \dot{O}\dot{O}\dot{O}H \rightleftharpoons O * \dot{C}HOC * \dot{O}\dot{O}\dot{O}H + \dot{O}H$	2.89E + 10	0.0	21863.0	[6]
$HOOCH_2OC * \dot{O}\dot{O}\dot{O} \rightleftharpoons O * \dot{C}HOC * \dot{O}\dot{O}\dot{O}H + \dot{O}H$	2.48E + 11	0.0	20900.0	[53]
$O * \dot{C}HOC * \dot{O}\dot{O}\dot{O}H \rightleftharpoons CO_2 + \dot{O}CHO + \dot{O}H$	1.05E + 16	0.0	41600.0	[6]
$cyOCH_2OC * O + \dot{H} \rightleftharpoons \dot{C}HOOCO + H_2$	4.80E + 08	1.5	2005.0	[6]
$cyOCH_2OC * O + \dot{O}H \rightleftharpoons \dot{C}HOOCO + H_2O$	2.40E + 06	2.0	-1192.2	[6]
$cyOCH_2OC * O + \dot{H}\dot{O}_2 \rightleftharpoons \dot{C}HOOCO + H_2O_2$	4.00E + 12	0.0	12976.7	[6]
$\dot{O}CHO + CO \rightleftharpoons \dot{C}HOOCO$	1.08E + 07	1.6	5588.0	$CH_3\dot{O} + CO$ [39]
$\dot{H}\dot{C}O + CO_2 \rightleftharpoons \dot{C}HOOCO$	2.92E + 06	1.6	36591.0	$\dot{C}H_3 + CO_2$ [39]

Table 6

Arrhenius parameters for reactions of the methyl formate submechanism; Low temperature. “*” and “cy” denote the C=O and cyclic ether functionalities respectively, † *this study*.

4 Computational Simulations

The modeling computations in this study were carried out using the *Chemkin 2* suite of programs (*SENKIN* and *PREMIX*) [57]. The fundamental modeling assumptions used in comparing the kinetic calculations with experiments are as follows:

4.1 Shock tube

Shock tube simulations are zero-dimensional and begin at the onset of the reflected shock period assuming constant volume and homogeneous adiabatic conditions behind the reflected shock wave. The reflected shock pressure and temperature are inputted as the initial pressure and temperature respectively and the simulated ignition delay time is defined as the time at which the maximum value of $[\dot{\text{C}}_2\text{H}] \times [\dot{\text{O}}]$ occurs. The current model does not include any reactions to account for emission from the electronically excited CH^* species which is measured experimentally. Therefore, in order to simulate the shock tube ignition delay times we use the relation established by Horning et al. [58] which states that the rate of emission from CH^* can be inferred from the rate of production of CH^* :

4.2 Variable pressure flow reactor

Although the net chemical reaction studied in the VPFR is exothermic, the deliberately fuel dilute nature of the reacting mixtures limits the departure of the temperatures reached due to chemical reaction from the initial temperature to ≤ 50 K for all VPFR experiments reported here. Thus, the reacting gas temperatures are closely approximated by the reactor wall temperatures, which are held at the initial reaction temperature. This approximation allows for the reaction to proceed in the test section under essentially adiabatic conditions. High convective velocities in the test section suppress spatial gradients and permit neglect of the diffusive terms in the governing equations. The experiment can therefore be modeled as a zero-dimensional system with isobaric and adiabatic approximations [30].

In the present experiments MF is observed to be converted to methanol and carbon monoxide at the earliest residence times observed. For example, the stoichiometric condition shows $\approx 30\%$ of the fuel to be converted directly to $\text{CH}_3\text{OH} + \text{CO}$ at a residence time of only 0.02 seconds, with only trace oxi-

dation products observed, Figure 5. The conical diffuser is composed of foam silica. Considering the establishing literature [2, 21, 59–62] regarding the problematic use of this material in controlled oxidation experiments for oxygenated fuels, we take the high levels of $\text{CH}_3\text{OH} + \text{CO}$ at residence times corresponding to sampling distances inside the diffuser to be evidence of the wall catalysed (heterogenous) decomposition of fuel. In order to compare this data to the predictions of a gas phase chemical kinetic model this effect must be accounted for. It is necessary to estimate the radical population inside the diffuser owed to the accelerated rate of the reaction $\text{MF} \rightleftharpoons \text{CH}_3\text{OH} + \text{CO}$. We do this by performing a quasi-steady-state calculation which is constrained by the known (measured) species concentrations at the earliest residence time analysed, this technique is described previously by Li et al. [56] and thoroughly by Zhao et al. [30]. The species output from this calculation is then used as input to *SENKIN* [57] and the simulation is continued under isobaric and adiabatic assumptions.

4.3 Laminar burning velocities

The laminar burning velocities were calculated by simulating freely propagating flames using the *PREMIX* [57] module considering multicomponent transport and thermal diffusive effects. Simulations were performed over a constant domain size ranging from -5cm to 5cm. The use of fifteen hundred grid points assures that stringent increments of 0.01 for both *CURV* and *GRAD* may be met and that the reported solutions are independent of grid size. The computed burned gas temperature of these simulations closely approximate the independently calculated adiabatic flame temperature, indicating that a true solution has been found.

All Figures in this study depict experimental measurement as symbols and kinetic modeling simulation as lines.

5 Results and Discussion

5.1 Variable pressure flow reactor

Methanol (CH_3OH), formaldehyde (CH_2O) and methane (CH_4) were observed as the major intermediates formed from the oxidation of MF in the flow reactor study. Reactants (MF and oxygen) were also quantified while the products, carbon dioxide (CO_2), carbon monoxide (CO) and water (H_2O) are observed to be formed as fuel and oxidizer are consumed, Figures 4–6.

Fig. 4. Flow reactor data (symbols) and simulations (heavy lines) for conditions of 0.005/0.02/0.975 MF/O₂/N₂, $\phi = 0.5$ at 3.0 atm and 900 K. ■ — MF, ■ — O₂, ▲ — CO, ● — H₂O, ● — CO₂, ▲ — CH₃OH, ● — CH₂O and ● — CH₄.

Fig. 5. Flow reactor data (symbols), simulations (heavy lines) and simulations assuming no wall catalysed decomposition of fuel (light lines) for conditions of 0.005/0.01/0.985 MF/O₂/N₂, $\phi = 1.0$ at 3.0 atm and 900 K. ■ — MF, ■ — O₂, ▲ — CO, ● — H₂O, ● — CO₂, ▲ — CH₃OH, ● — CH₂O and ● — CH₄.

Compared in the same Figures are model simulations (heavy lines) against those species measured during the oxidation of MF at 3 atm and ≈ 900 K in the flow reactor. In no case was the input fuel fraction recovered. In fact at the earliest residence time (0.02s), for all conditions studied only $\approx 75\%$ of the initial fuel fraction remained. Observe that high levels of methanol and carbon monoxide are present very early in reaction over all conditions. We note that the measured MF and methanol concentrations at a residence time of ≈ 0.05 seconds for each set of conditions are approximately equal, therefore what ever process is responsible for the early conversion of fuel is independent of oxygen concentration; characteristic of a heterogenous process. When this effect is accounted for by the described reinitializing technique, the modeling computations are in broadly good agreement with experiment, though the model over predicts MF reactivity at longer residence times for the $\phi = 1.5$ condition, Figure 6.

The lighter lines in Figure 5 show the model agreement assuming no catalytic wall effect occurs.

Fig. 6. Flow reactor data (symbols) and simulations (heavy lines) for conditions of 0.005/0.067/0.988 MF/O₂/N₂, $\phi = 1.5$ at 3.0 atm and 900 K. ■ — MF, ■ — O₂, ▲ — CO, ● — H₂O, ● — CO₂, ▲ — CH₃OH, ● — CH₂O and ● — CH₄.

Analysis of the chemistry occurring in the flow reactor shows that MF is primarily consumed by hydrogen abstraction reactions with a smaller but significant contribution from concerted elimination reactions. Specifically over the residence time of 0–0.7 seconds, the kinetic model shows that the radical species responsible for fuel consumption by hydrogen abstraction are $\dot{\text{H}}$ atom (40.1%), $\dot{\text{OH}}$ (37.2%) and HO_2 (1.9%) radicals and $\ddot{\text{O}}$ (1.8%) atom, with abstraction from the methyl site to form the $\dot{\text{C}}\text{H}_2\text{OCHO}$ species accounting for 54% of total fuel consumption *verses* 27.6% of fuel forming the $\text{CH}_3\dot{\text{O}}\text{CO}$ radical. The model shows the concerted elimination channels of $\text{MF} \rightleftharpoons \text{CH}_4 + \text{CO}_2$ and $\text{MF} \rightleftharpoons \text{CH}_3\text{OH} + \text{CO}$ to be important, accounting for 2.7% and 15.8% of total fuel consumption respectively. Indeed the concerted process of $\text{MF} \rightleftharpoons \text{CH}_3\text{OH} + \text{CO}$ accounts in total for methanol formation, while the slower reaction forming methane and carbon dioxide accounts for 15.5% of total methane formation. This reaction is almost completely responsible for that methane formed at early residence times, before the radical recombination reactions of $\dot{\text{C}}\text{H}_3 + \text{HO}_2 \rightleftharpoons \text{CH}_4 + \text{O}_2$ and $\dot{\text{C}}\text{H}_3 + \text{H}_2 \rightleftharpoons \text{CH}_4 + \dot{\text{H}}$, which are jointly responsible for the majority of methane production at later residence times become more significantly active.

The decomposition of the $\text{CH}_3\dot{\text{O}}$ and $\text{CH}_2\dot{\text{O}}\text{H}$ radicals, which are produced from methanol oxidation account for $\approx 60\%$ of the formaldehyde produced. The remaining formaldehyde fraction is produced by the decomposition of the $\dot{\text{O}}\text{CH}_2\text{O}_2\text{H}$ radical which is formed by the low temperature reaction sequence of:

which the model shows to be active at the temperatures (900 K) of the flow reactor study.

Fig. 7. Sensitivity coefficients to dT/dt for flow reactor simulation of the $\phi = 1.0$ condition at a residence time of 0.4 seconds.

To evaluate the significance that the estimated error in the assigned rate constants of the MF submechanism exert on the simulation of the flow reactor conditions, a first order sensitivity analysis [57] has been performed with dT/dt as the sensitive parameter. Any reaction responsible for increasing the temperature of the reacting flux shows a positive sensitivity coefficient (Σ) while the reactions responsible for inhibiting temperature rise display a negative Σ value. Figure 7 shows those reactions which have the largest influence over dT/dt at a residence time of 0.4 seconds and therefore identifies the reactions which have the largest influence on the overall chemical reactivity of the flow reactor simulation. Figure 7 shows that the system is dominated by hydrogen peroxide chemistry, with the chain branching reaction $\text{H}_2\text{O}_2 + \text{M} \rightleftharpoons \dot{\text{O}}\text{H} + \dot{\text{O}}\text{H} + \text{M}$ the most sensitive in the system.

Because the $\dot{\text{H}}\text{O}_2$ radical is abundant the sensitivity analysis shows its reaction to be of importance to the overall oxidation reaction. Those reactions of the $\dot{\text{H}}\text{O}_2$ radical which propagate the radical chain have a positive sensitivity coefficient (Σ), particularly if they result in H_2O_2 formation. Three individual reactions are responsible for $\dot{\text{H}}\text{O}_2$ formation at these conditions;

where the $\dot{\text{H}}\text{CO}$ radical is formed by formaldehyde oxidation, and the $\dot{\text{O}}\text{CH}_2\text{O}_2\text{H}$ radical by the low temperature $\dot{\text{R}}\text{O}_2$ pathway as outlined above.

Those chain terminating reactions of the $\text{H}\dot{\text{O}}_2$ radical inhibit the global oxidation reaction and so show negative values of Σ , Figure 7. In terms of the MF submechanism, Figure 7 shows that hydrogen abstraction from the methyl position to produce the $\dot{\text{C}}\text{H}_2\text{OCHO}$ radical leads to a more reactive system than if hydrogen abstraction is from the carbonyl position. This is so as the consumption of the $\dot{\text{C}}\text{H}_2\text{OCHO}$ radical produces the formyl radical and formaldehyde. Formaldehyde is further oxidized to produce more radical species, conversely the $\text{CH}_3\text{O}\dot{\text{C}}\text{O}$ radical predominantly decomposes to form a methyl radical and carbon dioxide, of which only the methyl radical plays further part in the global oxidation reaction.

5.2 Shock tube

Fig. 8. MF ignition delay times at a reflected shock pressure of $2.7 \text{ atm} \pm 0.4$ with error bars of $\pm \approx 7 \text{ K}$. ● — MF/ O_2 /Ar, 0.5/1.0/98.5, $\phi = 2.0$ and ● — MF/ O_2 /Ar, 0.5/2.0/97.5, $\phi = 1.0$. Dashed lines show predictions using parameters of Francisco [12] and Good and Francisco [14] (see text).

The performance of the kinetic model against shock tube ignition data is presented in Figures 8 and 9. Each set of ignition delays show Arrhenius temperature dependence. At 2.7 atm (Figure 8), the experimental data show only a slight effect of O_2 concentration at constant fuel concentration. The kinetic model does reproduce this effect but shows a stronger dependence on

O₂ concentration than observed in experiment.

Fig. 9. MF ignition delay times with error bars of $\pm \approx 7$ K. $\blacktriangle$ — MF/O₂/Ar, 0.5/2.0/97.5, $\phi = 0.5$, 5.4 atm ± 0.4 and $\bullet$ — MF/O₂/Ar, 2.5/5.0/92.5, $\phi = 1.0$, 9.4 atm, ± 0.4 .

The model reproduces the effect of pressure as observed in experiment quite well. However, agreement against the 5.4 atm data set is fair, with the simulations consistently faster than experiment and deviating increasingly with increase in reflected shock temperature. In the worst case the ignition delay is under predicted by almost a factor-of-two.

Ignition delay data were obtained from a total of 60 experiments for the mixtures listed in Table 1. To parameterize the performance of the kinetic model against these data, the ignition delay was simulated on a case-by-case basis using the specific reflected shock pressure, reflected shock temperature, and reactant concentration conditions of each experiment. Both measured and simulated ignition delay times were correlated using least-squares regression analyses to provide ignition delay time expressions as a function of pressure, temperature, and oxygen mole fraction. These parameters were chosen as they were individually sufficiently varied in the experiments. This is in contrast to fuel concentration which was omitted from the correlations as no reliable ignition time dependency on this parameter can be discerned from the dataset, see Table 1. The following correlations were obtained:

$$\tau_{\text{experiment}}(\mu\text{s}) = 10^{-2.74 \pm 0.25} p^{-0.67 \pm 0.14} X_{\text{O}_2}^{-0.46 \pm 0.09} \exp\left(\frac{30,569 \pm 582 \text{ cal mol}^{-1}}{RT}\right) \quad (4)$$

$$\tau_{model}(\mu s) = 10^{-4.85 \pm 0.11} p^{-0.48 \pm 0.06} X_{O_2}^{-0.96 \pm 0.04} \exp\left(\frac{38,116 \pm 252 \text{ cal mol}^{-1}}{RT}\right) \quad (5)$$

where p is pressure in atmospheres, X_{O_2} is the oxygen mole fraction, R is the universal gas constant, and T is the temperature in Kelvin. The standard error for each of the fitted parameters is shown and it is noted that the r-squared values for these correlations were in excess of 0.98.

These correlations have been used to normalize all measured and simulated ignition delay times to a common condition of 5 atm and 2% O_2 , which approximately correspond to average values over the entire dataset, Figure 10. It can be seen that the model represents the data well, only deviating at extreme low and high temperatures, in any case model-experiment discrepancies are always within a factor-of-two.

Fig. 10. Normalized ignition delay times to conditions of 2% O_2 and 5 atm. ● normalized experiment and — experimental correlation, ○ normalized simulation and — simulation correlation.

However, the model does show a higher activation energy by approximately 25%, $38.1 \text{ kcal mol}^{-1}$ compared to $30.5 \text{ kcal mol}^{-1}$ for experiment. This disparity is consistent with the stronger dependence on oxygen concentration displayed by the model compared to experiment, as exhibited by coefficients of 0.96 for model *verses* 0.46 for experiment, Equations 5 and 4 respectively. In addition though of lesser importance, the model also shows a weaker dependence on pressure than experiment, Equations 4 and 5. We return to discuss the chemical kinetic reasons for these discrepancies later. But some basic in-

sight can be gleaned by comparison against values reported in the literature for other fuels over similar conditions;

The activation energy of $\approx 30 \text{ kcal mol}^{-1}$ (Equation 4), of these MF ignition data is considerably lower than reported values for alkanes [58, 64] as well as other oxygenates, including alcohols, [65, 66] ethers [68], and esters [15] which show activation energy barriers in the region of 35–45 kcal mol^{-1} at similar high temperature conditions. The higher global activation energy barriers for these fuels are a result of the typical high temperature, hydrogen abstraction-alkyl radical β -scission, radical chain reaction oxidation mechanism. The empirical implication of the much lower activation energy barrier for the global oxidation reaction of MF is of a significantly different mechanism of oxidation than that which is accepted as typical at high temperature.

Further insight may be gained by a specific comparison to the reported high temperature ignition behavior of other ester fuels. Dooley [15] reports a canonical expression of

$$\tau_{\text{experiment}}(\mu\text{s}) = 6.92 \times 10^{-05} [\text{MB}]^{0.238 \pm 0.028} [\text{O}_2]^{-0.897 \pm 0.028} \exp\left(\frac{43,656 \pm 639}{RT}\right) \quad (6)$$

for the high temperature autoignition of the *n*-alkyl ester methyl butanoate (MB). An accompanying kinetic model reveals the high temperature oxidation mechanism of methyl butanoate to be a complex radical chain reaction, with only a very slight contribution from a six-centred concerted elimination reaction. Note that MB shows a substantially larger activation energy and approximately twice the value for oxygen dependence which we report for MF, Equation 4 *verses* Equation 6.

By contrast the high temperature oxidation mechanism of the ethyl ester, ethyl propanoate (EP) has been shown to occur overridingly through a low activation-energy concerted elimination reaction, Metcalfe [63] presents a canonical expression of

$$\tau_{\text{experiment}}(\mu\text{s}) = 9.773 \times 10^{-04} [\text{EP}]^{0.158 \pm 0.047} [\text{O}_2]^{-0.723 \pm 0.034} \exp\left(\frac{33,897 \pm 633}{RT}\right) \quad (7)$$

for the high temperature ignition of ethyl propanoate.

From Equation 7 and Equation 4, the empirically observed activation energies for the ignition of ethyl propanoate and MF share a considerably lower activation energy than for other hydrocarbon and oxygenated hydrocarbon systems. For analysis and explanation of ethyl propanoate oxidation see the works of Metcalfe et al. [63, 74, 75].

A chemical flux analysis of the MF kinetic model has been performed and shows that this shared global attribute does indeed betray a similarity in the respective high temperature oxidation mechanisms of these ester fuels.

Analysis of the chemically reacting flux of a shock tube simulation of MF for conditions of 1450 K and 2.7 atm for the stoichiometric case (Mixture 1) reveals that 95% of the initial fuel fraction is consumed in the first 50 μs , Figure 11.

Fig. 11. Major species profile for shock tube simulation of MF/O₂/Ar, 0.5/1.0/98.5, $\phi = 1.0$, at 2.7 atm and 1450 K. — MF, — CO, — CH₃OH, — CO₂, — CH₄, — CH₂O and — H₂.

The simulated and measured ignition delays for this condition are 353 and 334 μs respectively. During this time only two reactions are responsible for $\approx 98\%$ of fuel consumption; $\text{MF} \rightleftharpoons \text{CH}_3\text{OH} + \text{CO}$ and $\text{MF} \rightleftharpoons \text{CH}_4 + \text{CO}_2$ in approximately an 82:16 split with fission reactions accounting for $\approx 0.5\%$ of MF consumption. Due to the activity of the concerted elimination channels hydrogen abstraction reactions play only a very minor role in fuel consumption with hydrogen abstraction by $\dot{\text{H}}$ atom the largest contributor, accounting for 1% of total fuel consumption.

A sensitivity analysis to the simulated ignition delay time has also been performed employing the brute force technique [67]. We compute the ignition delay which results from individually increasing and decreasing each rate constant of the kinetic model by a factor-of-two. The sensitivity coefficient (Σ) is defined as

$$\Sigma = \text{Ln} \left(\frac{\tau_{\text{increased}} / \tau_{\text{decreased}}}{\text{Ln} 4} \right)$$

where $\tau_{\text{increased}}$ is the simulated ignition delay time computed by the factor-of-two increase in rate constant and $\tau_{\text{decreased}}$ is the simulated ignition delay

Fig. 12. Sensitivity coefficients to dT/dt at the time corresponding to 50% of the simulated ignition delay time for shock tube simulations of 0.5 % MF in Ar; ■ 1450K, 2.7 atm, $\phi = 1.0$, ■ 1450K, 2.7 atm, $\phi = 2.0$, ■ 1600 K, 5.4 atm, $\phi = 0.5$ and ■ 2.5 % MF 1600 K, 9.4 atm, $\phi = 1.0$.

time computed by the factor-of-two decrease in rate constant.

Figure 12 shows the largest sensitivity coefficients. Reactions with a negative sensitivity coefficient (Σ) effect a lengthening of the ignition delay time (inhibits reactivity) and reactions with positive Σ values indicate that a reaction shortens the ignition delay time (increases reactivity).

Consistent with the high temperature oxidation kinetics of hydrocarbons [19] and other oxygenates, including ethyl propanoate [74] the reaction of largest sensitivity over all conditions in MF oxidation is the radical chain branching reaction of $\dot{H} + O_2 \rightleftharpoons \ddot{O} + \dot{OH}$. Considering the above analyses of the chemical flux, (Figure 11 and Table 7), unsurprisingly, there are few reactions of the MF submechanism which have a large influence on the reactivity of the system. The majority of the sensitive reactions belong to the established $CH_3OH \rightarrow CH_2O \rightarrow HCO \rightarrow \dot{H}$ and $CH_4 \rightarrow \dot{C}H_3$ oxidation pathways, the chemical kinetic details of which are well established [29, 70]. The important point in this regard is that methanol (totally) and the majority of the methane produced, result from the activities of the concerted elimination reactions of MF.

To help explain these sensitivity coefficients the chemical reactions responsible

Reaction	% contribution to MF consumption			
	( ) $\phi = 1.0$	( ) $\phi = 2.0$	( ) $\phi = 0.5$	( ) $\phi = 1.0$
	1450 K 2.7 atm	1450 K 2.7 atm	1600 K 5.4 atm	1600 K 9.4 atm
$\text{MF} \rightleftharpoons \text{CH}_3\text{OH} + \text{CO}$	77.7	77.8	76.9	72.0
$\text{MF} \rightleftharpoons \text{CH}_4 + \text{CO}_2$	20.3	20.3	18.9	17.1
$\text{MF} + \dot{\text{H}} \rightleftharpoons \dot{\text{R}} + \text{H}_2$	1.2	1.2	2.0	5.5
$\text{MF} + \dot{\text{X}} \rightleftharpoons \dot{\text{R}} + \text{XH}$	0.5	0.4	2.0	5.0

Table 7

MF consumption in simulation of shock tube ignition delay times, where $\dot{\text{X}}$ is an abstracting radical $\neq \dot{\text{H}}$ atom and $\dot{\text{R}}$ is the $\dot{\text{C}}\text{H}_2\text{OCHO}$ and CH_3OCO radicals.

for fuel consumption for each analysed condition are presented in Table 7.

The sensitivity coefficients for the concerted elimination reactions at 1450 K and 2.7 atm (, $\phi = 1.0$ and , $\phi = 2.0$), Figure 12, show these reactions to have opposing effects on the global oxidation reaction; $\text{CH}_3\text{OH} + \text{CO}$ formation promoting reactivity and $\text{CH}_4 + \text{CO}_2$ formation inhibiting. This is the case as these reactions are effectively competing only with each other for fuel consumption, Table 7. The methanol oxidation pathway as outlined above produces higher numbers of reactive radicals than the methane oxidation pathway and hence the observed Σ values.

Table 7 shows that at the higher temperature of 1600 K hydrogen abstraction reactions are much more competitive in terms of fuel consumption than at 1450 K. At 1600 K the model shows that the mechanism of MF oxidation begins to switch away from a molecular elimination mechanism to a radical chain reaction mechanism. At these higher temperatures the concerted elimination reactions actually become inhibitive to the global oxidation reaction as their activity introduces chemically inert CO and CO_2 and the relatively unreactive CH_4 directly in to the system, slowing the growth of the radical pool.

The sensitivity coefficients for the high pressure-high fuel concentration condition ( ) show that $\text{CH}_3\text{OH} + \text{CO}$ formation has only a slight inhibiting effect, while $\text{CH}_4 + \text{CO}_2$ formation actually promotes reactivity at this condition.

This exceptional behavior may be explained by analysis of the reactions responsible for fuel consumption, Table 7. At this condition the model shows that hydrogen abstraction reactions account for a much larger percentage (10.5%) of fuel consumption than at any other condition and therefore the make-up of the chemical flux is more significantly dependent on hydrogen abstraction reactions than at any other condition.

In this regard, the C—H bonds of methane are much more strongly bound than those of methanol, and so the rate of hydrogen abstraction is much slower from methane than from methanol. Therefore the production of methanol results in

the consumption of more $\dot{\text{H}}$ atoms than does the production of methane. Since these channels are in direct competition both with each other, and with the hydrogen abstraction reactions for the consumption of fuel, the production of $\text{CH}_3\text{OH} + \text{CO}$ slows the growth of the radical pool due to a greater inhibition of the chain branching reaction $\dot{\text{H}} + \text{O}_2 \rightleftharpoons \ddot{\text{O}} + \dot{\text{O}}\text{H}$ than does the formation of $\text{CH}_4 + \text{CO}_2$. Hence the observed positive Σ value for $\text{CH}_4 + \text{CO}_2$ formation.

Through the presented chemical flux analysis we have shown that at the high temperatures of the shock tube experiments the low activation energy barriers assigned to the concerted elimination channels have a dramatic effect very early in the induction period of MF/O₂/Ar mixtures. The model shows that the propensity of these reactions is such, that in essence, a mixture of methanol/carbon monoxide and methane/carbon dioxide is being oxidized. It seems prudent therefore to evaluate the work of Francisco [12] against this experimental data.

The dashed lines in Figure 8 show simulated ignition delays for the 0.5% fuel, $\phi = 1.0$ and $\phi = 2.0$ mixtures at 2.7 atm performed with the described kinetic model but with the following modifications;

- the estimated activation energies for the reactions $\text{MF} \rightleftharpoons \text{CH}_3\text{OH} + \text{CO}/\text{CH}_4 + \text{CO}_2$ have been substituted with those values calculated by Francisco [12] i.e., 75 and 85 kcal mol⁻¹ respectively, our estimated A -factors have been retained.
- a third elimination reaction is considered, $\text{MF} \rightleftharpoons \text{CH}_2\text{O} + \text{CH}_2\text{O}$ is assumed to have a rate expression of $8.00 \times 10^{12} \exp(-77,800 \text{ cal mol}^{-1}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ which comprises an estimated A -factor and the calculated activation energy of Francisco.
- since the higher activation energy barriers of Francisco have the effect of making the hydrogen abstraction pathways much more competitive in terms of fuel consumption, it seems fair to also include in the modified kinetic model the rate constants for hydrogen abstraction from MF by $\dot{\text{H}}$ atom, $\dot{\text{O}}\text{H}$ and $\dot{\text{C}}\text{H}_3$ radicals as calculated by Good and Francisco [14].

It can be seen that the modified kinetic model predicts a larger global activation energy for MF oxidation than observed in experiment or predicted by the unmodified model.

The principles used in explanation of the sensitivity analysis of the unmodified model, may also be applied to the modified model. The lower temperature ignition delays are over-predicted by the modified kinetic model as the higher barriers to elimination slow fuel consumption at lower temperatures. From the sensitivity analyses of the unmodified model it is clear that at the lower temperatures of the shock tube study, methanol production has the effect of promoting reactivity. The higher barrier to methanol production of Francisco, precludes its formation in the modified model and hence a less reactive system

is effected, as evidenced by longer ignition delays.

The under-prediction of ignition delay at higher temperatures is due to the over-activity of the MF oxidation pathway. Specifically, the lower rate constants of the concerted elimination pathways in the modified model allow the hydrogen abstraction array to be the dominant mode of fuel consumption, consuming $\approx 65\%$ of fuel *verses* $\approx 6\%$ in the unmodified model. This allows the radical pool to become establish earlier in the induction period, producing shorter ignition delays. We conclude that the reported ignition delay data is not consistent with the activation energy barriers of the MF elimination reactions as calculated by Francisco [12].

In summary over all shock tube conditions the kinetic model shows concerted elimination reactions producing methanol/carbon monoxide and methane/carbon dioxide to consume the vast majority of the fuel fraction very early in the induction period. The activity of these reactions are responsible for the low global activation energy of MF oxidation of ≈ 38 kcal mol $^{-1}$ shown by the model.

Due to the propensity of their occurrence (see Table 7) and complicated and opposing effects on the simulated ignition delay time (see Figure 12), more precise agreement of modeling simulation with these shock tube ignition delays requires an accurate knowledge of the rate constants for both described concerted elimination channels of MF as a function of pressure as well as a function of temperature.

The reported values for the activation energy barrier for the reaction of $\text{MF} \rightleftharpoons \text{CH}_3\text{OH} + \text{CO}$ are 48–50 kcal mol $^{-1}$ from experiment [8–10] and 75–77 kcal mol $^{-1}$ from quantum chemical computation [12]. Given this considerable uncertainty we have made no attempt to adjust our description of the discussed concerted elimination reactions of MF from our initial estimates. However, we have shown that the evaluation of the available literature data on the similar processes of other chemical systems is sufficient to achieve a satisfactory level of agreement against experiment. Suffice it to say though certainly not precise, the rate constants which describe both concerted elimination reactions are correct in an approximate manner.

5.3 *Freely propagating laminar flames*

The laminar burning velocities (s_u^o) at 1 atm of MF/O $_2$ /N $_2$ mixtures are compared to model predictions as a function of equivalence ratio in Figure 13. Experiment shows that the value of s_u^o varies as a function of equivalence ratio from low values of ≈ 24 cm s $^{-1}$ at $\phi=0.8$ and $\phi=1.6$, to a peak value of 37.5 cm s $^{-1}$ at $\phi=1.2$. This general dependency of s_u^o on equivalence ra-

Fig. 13. Laminar burning velocities of MF/O₂/N₂ freely propagating flames at 1 atm ○ experiment and — simulation.

tio, with a peak to the fuel rich side of stoichiometric is similar to that seen for the burning velocities of hydrocarbons and the relatively fewer published measurements of oxygenates, for example see [71].

The model reproduces this data well, though predictions of s_u^o for the fuel leaner mixtures ($\phi = 0.8$ – 1.1) are consistently fast. Although the shock tube ignition data and this flame data share a common temperature regime of ≈ 1000 – 2000 K, the specifics of the chemistry of fuel consumption are different. While in the shock tube the model shows MF to be immediately consumed by concerted elimination reactions, MF oxidation chemistry in the flames is dominated by bimolecular reactions. For example at the peak burning velocity condition of $\phi=1.2$, the model shows that abstraction reactions by $\dot{H}$ atom (47.1%), $\dot{OH}$ radical (18.0%) and $\dot{O}$ atom (8.2%), consume a combined 73.3% of the initial fuel fraction across the flame front. Abstraction from the methyl position under these premixed flame conditions is again favored, 51% of fuel forming the $\dot{CH}_2OCHO$ species and 23.0% of fuel forming the $CH_3O\dot{C}O$ radical.

The concerted elimination reactions of fuel are shown to be competitive to a significant extent with hydrogen abstractions, $MF \rightleftharpoons CH_3OH + CO$ consumes 21.2% of fuel, while $MF \rightleftharpoons CH_4 + CO_2$ is responsible for 4.6% of fuel consumption. The model shows that despite the high temperature of this flame environment, which reaches a maximum of 2142 K for the $\phi=1.2$ case, the fission reactions of MF are of negligible importance, accounting for $\leq 0.2\%$ of total fuel

Fig. 14. Sensitivity coefficients to s_u^o for simulation of an atmospheric pressure MF/O₂/N₂, 0.112/0.187/0.701, $\phi = 1.2$ freely propagating flame.

consumption. Examination of the computed temperature profile shows that in fact at the point where 50% of the fuel has been depleted the flame temperature is only 1075 K. The first order dependence of the fuel decomposition rate constants shows that the fastest fission reaction, $\text{CH}_3\text{OCHO} \rightleftharpoons \dot{\text{C}}\text{H}_3 + \dot{\text{O}}\text{CHO}$ does not become competitive with the lower activation energy elimination reactions until temperatures of ≥ 1600 K. The kinetic model shows that at the point in the flame front where the temperature is equal to 1600 K, $\leq 0.1\%$ of the fuel fraction remains and hence the inactivity of the fuel fission reactions.

In order to evaluate the performance of the kinetic model in the simulation of the laminar burning velocities a first order sensitivity analysis [57] has been conducted with s_u^o as the sensitive parameter. Figure 14 shows normalized sensitivity coefficients to the laminar burning velocity for the simulation of the $\phi = 1.2$ case. Generally the sensitivity analysis is dominated by the reactions of $\dot{\text{H}}$ atom and $\dot{\text{O}}\text{H}$ radical.

As in the shock tube study the dominant high temperature chain branching reaction, $\dot{\text{H}} + \text{O}_2 \rightleftharpoons \ddot{\text{O}} + \dot{\text{O}}\text{H}$ exhibits the largest sensitivity coefficient (Σ). Unsurprisingly many of the most sensitive reactions involve small species chemistry which is described by the adopted base mechanism [30, 31]. Generally speaking, those reactions which terminate the radical chain display negative Σ values while radical chain branching reactions show positive Σ values. In terms of the MF chemistry developed in *this study* the sensitivity analysis raises a number of matters and shortcomings with the described MF chemistry.

Figure 14 shows the reaction $\dot{\text{H}} + \dot{\text{CH}}_2\text{OCHO} \rightleftharpoons \text{CH}_3\text{OCHO}$ to be important as a radical sink for $\dot{\text{H}}$ atom. Similarly the recombination of formyl and hydroxyl radicals to produce formic acid slows the global oxidation reaction in the flame. The kinetic model incorrectly approximates the rate constants for both of these reactions at the high pressure limit value as they are of minor importance in any of the other environments studied.

The decomposition of both alkyl radicals formed by hydrogen abstraction from MF are important in reproducing the measured laminar burning velocities. The decomposition of the CH_3OCO radical has been studied computationally [33,39]. Although the available rate constants for the sensitive $\text{CH}_3\dot{\text{O}} + \text{CO}$ reaction differ by approximately a-factor-of-two at 1400 K, the decomposition of the CH_3OCO radical may be considered well known in comparison to that of the more sensitive CH_2OCHO radical.

As is the case in the other regimes studied, the model shows the CH_3OCO radical to be consumed by β -scission reactions, forming $\dot{\text{CH}}_3 + \text{CO}_2$ and $\text{CH}_3\dot{\text{O}} + \text{CO}$ in a mean 78/22% split. The decomposition of the analogous $\dot{\text{CH}}_2\text{OCHO}$ species is slower, and the wide temperature range experienced across the flame front (298–2142 K) makes the chemistry of its consumption more complex, with typical low and high temperature pathways in competition. The reaction flux for the consumption of the CH_2OCHO radical is described in Table 8. Because the β -scission reaction is comparatively slow, the addition of molecular oxygen and radical–radical interactions contribute to CH_2OCHO consumption. The radical predominantly decomposes to produce formaldehyde and a formyl radical. This pathway, through the decomposition of the formyl radical is a major production channel for the important $\dot{\text{H}}$ atom, accounting for $\approx 20\%$ of total $\dot{\text{H}}$ atom production.

As the decomposition of the CH_3OCO radical predominately forms carbon dioxide, hydrogen abstraction from the carbonyl position of MF results in a less reactive system than hydrogen abstraction from the methyl position. Such is evident from Figure 14. The uncertainty in the presented kinetic description of the $\dot{\text{CH}}_2\text{OCHO}$ decomposition chemistry has been discussed. Examination of the competition between decomposition and isomerisation of the CH_2OCHO radical would remove much of the uncertainty in our description of MF oxidation.

The sensitivity of this reaction under the flame conditions of this study and the quality of agreement against the measured laminar burning velocities of MF/O₂/N₂e flames indicates that this description is approximately correct. Further evidence to this effect is presented by the comparisons of the same model against speciation data from a series of low pressure, fuel rich MF/O₂/Ar flames, in particular against the measured formaldehyde concentrations therein, see [72].

Reaction	% contribution to consumption
$\dot{\text{C}}\text{H}_2\text{OCHO} \rightleftharpoons \text{CH}_2\text{O} + \dot{\text{H}}\text{CO}$	63.8
$\dot{\text{C}}\text{H}_2\text{OCHO} + \text{O}_2 \rightleftharpoons \dot{\text{O}}\text{OCH}_2\text{OCHO}$	11.7
$\dot{\text{C}}\text{H}_2\text{OCHO} + \dot{\text{H}} \rightleftharpoons \text{CH}_3\text{OCHO}$	11.4
$\dot{\text{C}}\text{H}_2\text{OCHO} \rightleftharpoons \text{CH}_3\text{O}\dot{\text{C}}\text{O}$	5.4
$\dot{\text{C}}\text{H}_2\text{OCHO} + \dot{\text{C}}\text{H}_3 \rightleftharpoons \text{CH}_3\text{CH}_2\text{OCHO}$	3.5
$\dot{\text{C}}\text{H}_2\text{OCHO} + \text{H}\dot{\text{O}}_2 \rightleftharpoons \dot{\text{O}}\text{CH}_2\text{OCHO} + \dot{\text{O}}\text{H}$	2.0

Table 8

$\dot{\text{C}}\text{H}_2\text{OCHO}$ radical consumption for a MF/O₂/N₂, 0.112/0.187/0.701, $\phi = 1.2$ flame at 1 atm.

6 Conclusions

6.1 Methyl ester oxidation

The oxidation of methyl formate, the most basic methyl ester, has been studied across a range of combustion device relevant conditions. Mechanistic insight to methyl formate oxidation has been provided by the measurement of methanol, formaldehyde and methane as the major stable intermediates formed in a flow reactor study. The high temperature reactivity of methyl formate has been characterized as Arrhenius by measurement of ignition delay time over a variety of conditions in a shock tube study. From these measurements the activation energy of the high temperature oxidation of methyl formate has been determined to be $\approx 30 \text{ kcal mol}^{-1}$. We postulate that the exhibition of such a low activation energy barrier is evidence of a mechanism of fuel decomposition which is primarily non-radical in nature. In addition only a weak dependence of induction time on oxygen concentration was observed. The laminar burning velocity of methyl formate/air mixtures has been shown to be consistent with that of other hydrocarbons and oxygenates in that a parabolic dependence of burning velocity is observed as equivalence ratio is increased from $\phi = 0.8$ to $\phi = 1.6$, with the peak burning velocity observed at a value of $\phi = 1.2$.

A validated kinetic model shows that under the high temperature conditions of the shock tube study, methyl formate is consumed very early in the induction period by concerted elimination reactions of fuel, forming methanol/carbon monoxide and methane/carbon dioxide directly. The computational reproduction of the high temperature ignition delays are dependent to a large extent on the accurate description of these concerted elimination reactions. As such, we could not reconcile these experimental data with the activation energy barriers for these reactions which have been calculated by Francisco [12]. However

we do agree qualitatively with the basic conclusion of Francisco; that the formation of methanol and carbon monoxide is the dominant mode of MF decomposition at high temperatures.

Several other studies have noted that concerted elimination reactions play an important role in alkyl ester oxidation; six centred concerted eliminations produce ethene and an alkyl acid directly from ethyl ester fuels [7, 73–75], but the analogous reactions of n-alkyl methyl esters have been shown to be of little importance by both experiment [21, 74] and quantum chemical computation [73]. Moreover, the chemical kinetic study of ester oxidation by the methodical increase of the complexity of fuel molecular structure [7, 15], is complicated by the significant propensity of concerted elimination reactions specific to the molecular structure of each ester fuel. For example the important three-centred reaction which occurs for methyl formate forming methanol and carbon monoxide by cleavage of the C—H bond of the carbonyl carbon atom may not occur for alkyl esters as the C—H bond is replaced by a C—C bond in that generic molecular structure. In this regard the present kinetic mechanisms for methyl formate oxidation would benefit from the detailed mechanistic study of the oxidation of larger methyl esters such as methyl acetate, indeed *vice versa* and we note that such works are underway [7, 76].

Lastly, in developing the present methyl formate kinetic model attention has been given to the inclusion of low temperature oxidation pathways. The isomerization of alkylperoxy radicals formed at low-temperature have been describe in a manner consistent with parameters recently proposed for n-alkyl methyl esters [54]. The kinetic model predicts low temperature reactivity including a degree of negative temperature coefficient behavior for methyl foramte oxidation. However validation of the model at low temperature conditions has not been performed due to a lack of experimental data.

6.2 Estimation of the rate constants for hydrogen abstraction

The kinetic model tests a method for the estimation of the rates of hydrogen abstraction from those C—H bonds which are not of typical enthalpies for which rate constant data is available, but which are typical of, and central to, the accurate description of the oxidation of oxygenated/bio type molecules.

The direct observation of the stable species formed by β -scission from a radical species which has been produced by hydrogen abstraction from a fuel molecule is usually a direct indication as to the prevalence of hydrogen abstraction from a specific site on a parent fuel molecule. The species which result from this process in the case of methyl formate are; formaldehyde, carbon dioxide and carbon monoxide. The evaluation of the proposed method for the estimation

of rate constants for hydrogen abstraction is complicated as these are species which may be formed by a variety of pathways during the oxidation of any hydrocarbon fuel. The situation is further complicated by the formation of methanol as the largest intermediate species formed from methyl formate oxidation, as the oxidation pathway of methanol also involves the formation of formaldehyde and carbon monoxide as primary intermediates [30].

Thus the available intermediate species measurements do not stringently test our treatment of hydrogen abstraction from methyl formate. However the fuel chemistry which occurs in the freely propagating laminar flames is dependent to a large extent on radical abstraction reactions. Therefore the accurate prediction of the burning velocity measurements is dependent on an accurate description of the hydrogen abstraction reactions. Though seemingly adequate for the methyl formate system, the proposed procedure for the estimation of rate constants for hydrogen abstraction from unorthodox bond dissociation energies would benefit from further test. Particularly for application to those C—H bonds which are of much weaker bond strength than a typical secondary C—H bond.

In summary, the described kinetic model for methyl formate oxidation generally reproduces the global reactivity observed in experiment quite well and therefore indicates that the important rate constants for the oxidation of this small ester system, including hydrogen abstraction from fuel and alkyl radical β -scission have been accurately assigned. Moreover the most significant uncertainty in the kinetic model is likely in the rate constants describing the concerted elimination reactions of methyl formate, such that improvements in their description may improve model predictions of shock tube induction times in particular.

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References

1. A. Sinha, M. J. Thomson, Combust. Flame, 136 (2004) 548–556.
2. C.A. Daly, J.M. Simmie, P. Dagaut, M. Cathonnet, Combust. Flame 125 (2001) 1106–1117.

3. I. Liu, N.W. Cant, J.H. Bromly, F.J. Barnes, P.F. Nelson, B.S. Haynes, *Chemosphere* 42 (2001) 583–589.
4. S.M. Japar, T.J. Wallington, J.F.O. Richert, J.C. Ball, *Int. J. Chem. Kinet.* 22 (1990) 1257–1269.
5. M.S. Graboski, R.L. McCormick, *Prog. Energy Combust. Sci.* 24 (1998) 125–164.
6. E.M. Fisher, W.J. Pitz, H.J. Curran, C.K. Westbrook, *Proc. Combust. Inst.* 28 (2000) 1579–1586.
7. C.K. Westbrook, W.J. Pitz, P.R. Westmoreland, F.L. Dryer, M. Chaos, P. Osswald, K. Kohse-Hinghaus, T.A. Cool, J. Wang, B. Yang, N. Hansen, T. Kasper, *Proc. Combust. Inst.* 32 (2009) 221–228.
8. C.P. Davis, Ph.D. Thesis, University of Mississippi, Oxford, Mississippi 1983.
9. E. W. Steacie, *Proc. R. Soc. (London)* 127 (1930) 314–330.
10. D.V.S. Jain, B.S. Murwaha, *Indian J. Chem.* 7 (1969) 169–174.
11. R.C.I. Pereira, P.C. Isolani *J. Photochem. Photobiol A.* 42 (1988) 51–61.
12. J.S. Francisco, *J. Am. Chem. Soc.* 125 (2003) 10475–10480.
13. D.A. Good, J.S. Francisco, *J. Phys. Chem. A* 104 (2000) 1171–1185.
14. D.A. Good, J.S. Francisco, *J. Phys. Chem. A* 106 (2002) 1733–1738.
15. S. Dooley, Ph.D. Thesis, National University of Ireland, Galway 2008.
16. J.M. Smith, Ph.D. Thesis, National University of Ireland, Galway 2004.
17. J.M. Smith, J.M. Simmie, H.J. Curran, *Int. J. Chem. Kinet.* 37 (2005) 728–736.
18. P. Cadman, G.O. Thomas, P. Butler, *Phys. Chem. Chem. Phys.* 2 (2000) 5411–5419.
19. A. Lifshitz in: G. Ben-Dor, O. Igra, T. Elperin (Eds.), *Handbook of Shock Waves*, Vol.3. Academic Press, San Diego, 2001, p. 212–256.
20. C. Morley, <http://www.gaseq.co.uk/>
21. S. Dooley, H.J. Curran, J.M. Simmie, *Combust. Flame* 153 (2008) 1–52.
22. T.J. Held, F.L. Dryer, *Int. J. Chem. Kinet.* 30 (1998) 805–830.
23. X.Qin, Y. Ju, *Proc. Combust. Inst.* 30 (2005) 233–240.
24. G. Rozenchan, D.L. Zhu, C.K. Law, S.D. Tse, *Proc. Combust. Inst.* 29 (2002) 1461–1469.
25. M.P. Burke, Z. Chen, Y. Ju, F.L. Dryer, *Combust. Flame* 156 (2009) 771–779.
26. R.A. Strehlow, L.D. Savage, *Combust. Flame* 31 (1978) 209–211.
27. G.H. Markstein, *Non-Steady Flame Propagation*, New York, 1964, p. 22.

28. Z. Chen, M.P. Burke, Y. Ju, *Proc. Combust. Inst.* 32 (2009) 1253–1260.
29. J. Li, Z. Zhao, A. Kazakov, M. Chaos, F.L. Dryer, J.J. Scire Jr., *Int. J. Chem. Kinet.* 39 (2007) 109–136.
30. Z. Zhao, M. Chaos, A. Kazakov, F.L. Dryer, *Int. J. Chem. Kinet.* 10 (2008) 1–18.
31. D. Healy, H.J. Curran, J.M. Simmie, D.M. Kalitan, C.M. Zinner, A.B. Barrett, E.L. Petersen, G. Bourque, *Combust. Flame* 155 (2008) 441–448.
32. H.K. Hall Jr., J.H. Baldt. *J. Am. Chem. Soc.* 93 (1971) 140–145.
33. P.A. Glaude, W.J. Pitz, M.J. Thomson, *Proc. Combust. Inst.* 30 (2005) 1111–1118.
34. R. Sumathi, W.H. Green Jr., *Phys. Chem. Chem. Phys.* 5 (2003) 3402–3417.
35. NIST Chemistry WebBook, NIST Standard Reference Database Number 69, Eds. P.J. Linstrom and W.G. Mallard, March 2005, National Institute of Standards and Technology, Gaithersburg MD, 20899, <http://webbook.nist.gov>.
36. S.W. Benson in: *Thermochemical Kinetics*, 1976, John Wiley and Sons, Inc., New York.
37. E.R. Ritter, J.W. Bozzelli, *Int. J. Chem. Kinet.* 23 (1991) 767–778.
38. L.R. McCunn, K.C. Lau, M.J. Krisch, L.J. Butler, J.W. Tsung, J.J. Lin, *J. Phys. Chem. A* 110 (2006) 1625–1634.
39. L.K. Huynh, A. Violi, *J. Org. Chem.* 73 (2008) 94–101.
40. J.P. Orme, H.J. Curran, J.M. Simmie, *J. Phys. Chem. A* 110 (2005) 114–131.
41. R. Atkinson, D.L. Baulch, R.A. Cox, R.F. Hampson Jr., J.A. Kerr, M.J. Rossi, and J. Troe, *J. Phys. Chem. Ref. Data*, 26 (1997) 521–1011.
42. A.T. Droege and F.P. Tully, *J. Phys. Chem.* 90 (1986) 1949–1954.
43. F.P. Tully, J.E.M. Goldsmith and A.T. Droege, *J. Phys. Chem.* 90 (1986) 5932–5937.
44. J. Aguilera-Iparraguirre, H.J. Curran, W. Klopper, and J.M. Simmie, *J. Phys. Chem. A* 112 (2008) 7047–7054.
45. H.H. Carstensen, A.M. Dean and O. Deutschmann, *Proc. Combust. Inst.* 31 (2007) 149–157.
46. W. Tsang, R.F. Hampson, *J. Phys. Chem. Ref. Data* 15 (1986), 1087–1279.
47. R.R. Baldwin and R.W. Walker, *Symp. Int. Combust. Proc.* 17 (1979) 525–533.
48. M. Scott and R.W. Walker, *Combust. Flame* 129 (2002), 365–377.

49. NIST Standard Reference Database 17, Version 7.0 (Web Version), Release 1.4.2, Data Version 2009.01, <http://kinetics.nist.gov>
50. C. Sheng, J.W. Bozzelli, A.M. Dean, A.Y. Chang, *J. Phys. Chem. A* 106 (2002) 7276–7293.
51. H.J. Curran, *Int. J. Chem. Kinet.* 38 (2006) 250–275.
52. A. Rauk, R.J. Boyd, S.L. Boyd, D.J. Henry, L. Radom, *Can. J. Chem.* 81 (2003) 431–442.
53. H.J. Curran, P. Gaffuri, W.J. Pitz, C.K. Westbrook, *Combust. Flame* 114 (1998) 149–177.
54. C.J. Hayes, D.R. Burgess Jr., *Proc. Combust. Inst.* 32 (2009) 263–270.
55. S.L. Fischer, F.L. Dryer, H.J. Curran, *Int. J. Chem. Kinet.* 32 (2000) 713–740.
56. J. Li, A. Kazakov, F.L. Dryer, *Int. J. Chem. Kinet.* 33 (2001) 859–867.
57. R.J. Kee, G. Dixon-Lewis, J. Warnatz, M.E. Coltrin, J.A. Miller, Technical Report SAND86-8246, Sandia National Laboratories, Albuquerque, NM, 1986.
58. D.C. Horning, D.F. Davidson, R.K. Hanson, *J. Propul. Power.* 18 (2002) 363–371.
59. A. Goldaniga, T. Faravelli, E. Ranzi, P. Dagaut, M. Cathonnet, *Proc. Combust. Inst.* 27 (1998) 353–360.
60. J.C. Brocard, F. Baronnet, *Oxid. Commun.* 1 (1980) 321–327.
61. A. Ciajola, A. D’Anna, M. Kurz, *Combust. Sci. Tech.* 123 (1997) 49–61.
62. F.M. Haas, M. Chaos, F.L. Dryer, *Combust. Flame* *in press* 2009.
63. W.K. Metcalfe, Ph.D. Thesis, National University of Ireland, Galway 2008.
64. M.A. Oehlslaeger, D.F. Davidson, J.T. Herbon, R.K. Hanson, *Int. J. Chem. Kinet.* 36 (2003) 67–78.
65. C.T. Bowman, *Combust. Flame* 25 (1975) 343–354.
66. J.T. Moss, A.M. Berkowitz, M.A. Oehlschlaeger, J. Biet, V. Warth, P.A. Glaude, F. Battin-Leclerc, *J. Phys. Chem. A* 112 (2008) 10843–10855.
67. M. Frenklach in: W.C. Gardiner, Jr. (Ed), *Combustion Chemistry*, Springer-Verlag, New York. 1984, p. 440.
68. C.T. Bowman, D.M. Golden, R.K. Hanson, H. Pitsch, D.F. Davidson, A. Bardos, R. Cook, Z. Hong, P. Iyengar, S. Shashank, S. Vasu, K. Walters, R. Malhotra, GCEP Technical Report 2006; available at <http://gcep.stanford.edu/pdfs/>.
69. M. Chaos, A. Kazakov, Z. Zhao, F.L. Dryer, *Int. J. Chem. Kinet.* 39 (2007) 399–414.

70. G.P. Smith, D.M. Golden, M. Frenklach, N.W. Moriarty, B. Eiteneer, M. Goldenberg, C.T. Bowman, R.K. Hanson, S. Song, W.C. Gardiner Jr., V.V. Lissianski, Z. Qin, http://www.me.berkeley.edu/gri_mech/.
71. S. Pichon, G. Black, N. Chaumeix, J.M. Simmie, H.J. Curran, R. Donohue, *Combust. Flame* 156 (2009) 494–504.
72. S. Dooley, M. Chaos, F.L. Dryer, H.J. Curran, B. Yang, J. Wang, T.A. Cool, T. Kasper, N. Hansen, 6th U.S. National Combustion Meeting 2009.
73. A.M. El-Nahas, M.V. Navarro, J.M. Simmie, J.W. Bozzelli, H.J. Curran, S. Dooley, W. Metcalfe, *J. Phys. Chem. A* 111 (2007) 3727–3739.
74. W.K. Metcalfe, S. Dooley, H.J. Curran, J.M. Simmie, A.M. El-Nahas, M.V. Navarro, *J. Phys. Chem. A* 111 (2007) 4001–4014.
75. W.K. Metcalfe, C. Togbé, P. Dagaut, H.J. Curran, J.M. Simmie, *Combust. Flame* 156 (2009) 250–260.
76. P. Osswald, U. Struckmeier, T. Kasper, K. Kohse-Hinghaus, J. Wang, T.A. Cool, N. Hansen, P.R. Westmoreland, *J. Phys. Chem. A* 111 (2007) 4093–4101.

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Chemical-kinetic modeling of ignition delays: Considerations in interpreting shock tube data

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1. Introduction

Interest in the combustion characteristics of practical fuels and their surrogates at conditions relevant to those encountered in automotive as well as gas turbine engines has led to a number of recent shock tube studies involving high-density, undiluted fuel/air mixtures (e.g. [1-11]). These high pressure studies extend to relatively low temperatures (below ~ 1100 K), well below typical dilute shock tube investigations aimed at achieving fundamental kinetic information on elementary reactions or validating chemical kinetic models. The observations of chemical ignition delays that have emerged at these extended conditions are frequently used as validation data for developing insights to and detailed kinetic models for hydrocarbon oxidation chemistry, that encompass negative temperature coefficient (NTC) and hot ignition behavior, presenting valuable information for designers of combustions systems as well as modelers.

However, there has been an emerging concern about the interpretation of these shock tube data, most prominently raised by recent discussions concerning the ignition behavior of syngas mixtures [8]. There, similarities in ignition delay measurements from various shock tube, flow reactor, and rapid compression observations were noted to differ considerably from kinetic model predictions generated using homogeneous, zero-dimensional, isochoric modeling assumptions (i.e. constant internal energy, U , and volume, V) typically employed by kineticists. As a result, the fundamental understanding of syngas elementary chemical kinetics was brought

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into question. In considering these observations [12, 13], we emphasized that the high sensitivity of induction chemistry to any type of experimental perturbations or non-idealities is what principally led to similarities in observations amongst the various experimental venues. Furthermore we argued that disparities in observations and kinetic predictions were a result of the ideal modeling assumptions applied and their inability to represent experimental conditions appropriately. In the particular case of shock tube observations, we noted the multi-dimensional nature of the ignition event in the weak ignition regime where characteristic kinetic times are strongly influenced by induction chemistry involving HO_2 and H_2O_2 reactions, and we hypothesized a number of potential perturbing phenomena that would not be captured by modeling approaches that assume uniform, constant U , V (or constant enthalpy, H , and pressure, P) conditions in the reflected shock gases. Finally, noting that hydrocarbon ignition delay data at similar temperatures, pressures, and energy densities were also commonly treated in a similar ideal manner, we indicated that similar misinterpretations were likely to exist.

Recently, several papers have drawn attention to the fact that significant pressure variations can occur during ignition of syngas- as well as hydrocarbon-oxidizer mixtures featuring long ignition times (several milliseconds or longer). These revelations have significant impact on the arguments made with regard to syngas combustion as well as hydrocarbon model validation based upon shock tube data presently in the literature. This communication is intended to bring attention to these issues and to review and summarize their implications in interpreting and modeling ignition delay data collected in shock tubes, as well as species-time histories that may be observed subsequent to ignition.

2. Scrutiny of shock tube pressure-time histories

Shock-induced self-ignition of undiluted fuel/air mixtures at the conditions of interest noted above are characterized by relatively long ignition delay times on the order of a few milliseconds. The ignition event is accompanied by marked changes in pressure and heat release. Therefore, ignition under these conditions is strongly coupled to the thermodynamic state and fluid dynamics of the gas behind the reflected shock wave. Uni-dimensional analyses predict that the gas behind a reflected shock should be stationary and have uniform thermodynamic properties over the entire test volume. In the case of syngas/air mixtures, ideal analyses further predict that no significant pre-ignition heat release can occur without substantial depletion of reactants, voiding the philosophical definition of “ignition.” On the other hand, pre-ignition chemistry might occur in the case of hydrocarbons, as a result of negative temperature coefficient behavior (i.e. two-stage ignition), leading to observable radical production.

Practically, however, even for dilute mixture studies, unavoidable non-idealities exist in the shocked gases, due to the ubiquitous presence of boundary layers. Incident shock attenuation, boundary layer growth, and shock-wave/boundary-layer interactions lead to non-uniform pressures and temperatures behind the reflected shock which gradually increase with time [14-16]. Furthermore, residual gas velocities may exist behind the reflected shock wave which further lead to the establishment of pressure gradients along the shock tube axis [17, 18]. These non-idealities can be minimized by using large-diameter shock tubes, dilute fuel/oxidizer mixtures in monoatomic gases, and short test times (less than about 500 μ s) [14, 15, 18]. The latter two options, however, are not applicable to ignition studies of undiluted fuel/air mixtures.

For highly reactive mixtures the above phenomena are further compounded by the fact that at high pressures and lower temperatures, shock tube ignition is not homogeneous but rather

it initiates at localized “hot spots” in a deflagrative manner leading to a homogeneous transition to detonation [1, 19-22]. Gas expansion due to the finite exothermicity of the initial, localized, heterogeneous reaction sites induces further increases in pressure throughout the gases behind the reflected shock, prior to the main ignition event. These features are typical of the well-known mild ignition process recently reviewed in Refs. 12 and 13. For non-reactive mixtures, Petersen and Hanson [14] reported temperature increases (due to observed pressure gradients behind the reflected shock) of up to 40 K over 500 μ s for representative pressure and temperature ranges of 24-530 atm and 1275-1900 K, respectively. For conditions relevant to practical fuels (i.e. 25-50 atm and 700-1000 K) and due to their relatively long ignition times, more severe pressure and temperature increases should be expected.

From the discussion above, it is clear that changes in the thermodynamic state of the gas behind the reflected shock wave are likely to be significant and, thus, can have a pronounced effect on kinetic observations as well as the ignition process [12, 13]. Figure 1 shows pressure-time histories during ignition of several different fuel/air systems [1, 3, 5, 23]. Pressure increases of nearly a factor of two prior to ignition can be observed (see Figs. 1a and 1c). In such instances, kinetic modeling of ignition delay should no longer be performed under the common assumption that the shock tube behaves as a constant volume system with constant internal energy. The pressure history in these cases is needed; however, this information is rarely given in the available literature. Instead, most experimental shock tube studies offer sample pressure profile plots where the ordinate scaling chosen (large enough to capture pre- and post-ignition pressure values) is such that pressure increases prior to ignition are not evident.

Even though the aforementioned non-idealities present in shock tubes at the conditions of interest have been known for some time and noted by shock tube experimentalists [1, 3, 14-22],

recent shock tube studies of fuel/air mixtures have failed to identify these phenomena as having considerable impact on the reported data [4-11]. This, in addition to the lack of pressure-time history information noted above, has led both the shock tube and general chemical kinetic modeling communities to employ, erroneously, constant U , V assumptions in interpreting shock tube data. Exemplar of this fact is the study of Davidson et al. [5] who acknowledged the presence of the pre-ignition pressure rise seen in Fig. 1c and noted that existing kinetic models failed to predict this pre-ignition activity. However, Davidson et al. [5] considered this behavior to be due to a chemical-kinetic process and postulated that matching the pre-ignition pressure-time history (and associated heat release) would be a modeling constraint and a good validation test for chemical-kinetic models. The discussion above strongly suggests that the conclusions of Davidson et al. [5] are more a result of misinterpretations that the experimental data could be modeled as a constant U , V system than a shortcoming of the kinetic models.

Further evidence of such misinterpretations can be found in the study of Cadman et al. [24]. They reported a distinct decrease in the activation energy of propane-air ignition data for ignition times longer than approximately 1 ms. Such behavior could not be reproduced using available chemical-kinetic models. Cadman et al. [24] identified the importance of hydroperoxyl, propyl, and methyl radical chemistry which they considerably modified; the updated chemical-kinetic schemes, however, still could not reconcile the observed model-experiment differences. Furutani et al. [21, 22] reported similar changes in the activation energy of methane as well as iso-octane ignition delays as those shown by Cadman et al. [24]. Based on the results of Furutani et al., however, it is clearly evident that the change in the activation energy of the data at lower temperatures and longer ignition times, is solely due to the non-idealities discussed above rather than being dependent on chemical processes.

The issues outlined above have received considerable attention recently, evidenced by reports [25-29] where ignition delay data are further examined and pressure variations prior to ignition are identified and taken into account when interpreting and modeling the data. Their implications into how ignition delay chemical-kinetic modeling should be approached are discussed in the next section.

3. Chemical-kinetic modeling approaches

In several previous investigations, it has been suggested that pre-ignition pressure variations in reflected shock tube observations can be assumed to manifest in the system as polytropic processes [2, 3, 14, 15, 18]. Pressure histories and associated temperatures deduced from isentropic relations have been used by Fieweger et al. [2] to adjust iso-octane/air ignition data affected by pre-ignition pressure rise. Others [3, 25, 29] have opted to compute an effective or average pressure and temperature based on the observed pressure history and plot the data with respect to these adjusted values. The presence of dynamic pressure features prior to ignition, however, can have considerable effects on radical initiation processes, as discussed by Mittal et al. [30]. Therefore it is important to include measured pressure histories in modeling approaches rather than using averaged or effective values.

Li et al. [26] propose a specific modeling tool for shock tube applications, CHEMSHOCK, which allows for the treatment of time-varying pressures coupled with chemical kinetics. CHEMSHOCK solves the coupled energy and chemical species system of differential equations using a two-step process: at every time step the system is first solved assuming constant U , V conditions, and then pressure and temperature are adjusted isentropically to match the measured pressure profile while keeping the chemical composition fixed. Pang et al. [27]

showed promising results using CHEMSHOCK in modeling ignition delay data of H_2/O_2 mixtures, see Fig. 2.

We wish to point out, however, that there is no need for unique software to consider pressure variations in shock tube ignition delay predictions. SENKIN [31], part of the CHEMKIN-II [32] suite of programs, is completely capable of handling this situation. A time-dependent polytropic compression (or expansion) results in both volume and density changing with time. In contrast to other options such as CONP (constant enthalpy and pressure) and CONV (constant internal energy and volume, commonly used for shock tube modeling), the VTIM (i.e. volume as a function of time) option in SENKIN can be employed to emulate a time-dependent polytropic state change. The user must only provide time functions for variations in the specific volume of the system. Knowing the functional variation of pressure from measured data and assuming isentropic compression/expansion, the functions to be provided are:

$$\nu(t) = \frac{1}{\rho_0} \left[\frac{P(t)}{P_0} \right]^{-1/\gamma}$$

$$\frac{d\nu}{dt} = -\frac{1}{\gamma} \frac{\nu(t)}{P(t)} \frac{dP}{dt}$$

where ν is the specific volume, P the measured pressure, γ the specific heat ratio, and P_0 and ρ_0 are the initial pressure and density, respectively, behind the reflected shock wave. This approach has been successfully used in the modeling of rapid compression machine ignition and is further detailed in Ref. 33. Petersen and Hanson [14] also used a similar methodology to account for observed pressure variations behind reflected shock waves.

Figure 2 shows computations performed using both SENKIN and CHEMSHOCK against data collected by Pang et al. [27] for validation of the CHEMHOCK model. In the experiments, for $\text{H}_2/\text{O}_2/\text{Ar}$ (4/2/94 mol) mixtures, a linear pressure rise of about 2%/ms was observed for

pressure and temperature conditions of 3.3-3.7 atm and 924-1118 K, respectively. For consistency the present SENKIN chemical-kinetic calculations shown in Fig. 2 were performed using GRI-Mech 3.0 [34] and implementing the same updates for the heat of formation of OH [35] and the reaction $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$ [36] as those used by Pang et al. [27]. For ignition times less than approximately 1 ms, the SENKIN constant U , V model agrees fairly well with the data. At longer test times, the gradual pressure (and temperature) increase can have considerable effects on the ignition process, as noted above. In this case, Fig. 2 shows that the constant U , V approach fails to provide a good estimate of ignition delay for temperatures lower than 975 K. SENKIN modeling with VTIM assuming a linear pressure profile provides much improved predictions and yields very similar values to those computed with CHEMSHOCK.

Unlike the trends observed in the study of Petersen and Hanson [14] and Pang et al. [27], for higher concentrations of reactants (i.e. fuel/air mixtures) and due to the mild ignition processes discussed above, observed pressure rises are seldom linear, as shown in Fig. 1. In the case of toluene, the pressure traces shown in Fig. 1c can be used to further demonstrate the application of the SENKIN/VTIM approach described above. Davidson et al. [5] showed that an available toluene model [37] considerably over-predicted ignition delays of stoichiometric toluene/air mixtures (see Fig. 3) while providing reasonable results for lean mixtures. Fieweger et al. [1] indicated that significant pressure increases, like that shown in Fig. 1a, occurred for iso-octane/air mixtures only at stoichiometric conditions; toluene may, thus, exhibit similar behavior. Figure 3 shows the model-data discrepancies discussed by Davidson et al. [5]. Note, however, that data collected at 17 atm exhibit relatively short ignition delays at lower temperatures. This is not a result of chemistry leading to negative temperature coefficient behavior as toluene exhibits no such behavior [38]. Even though pressure profiles were not reported for the 17 atm

data [5] the traces shown in Fig. 1c for the 50 atm dataset indicate strong pre-ignition activity that cannot be approximated using a linear pressure increase assumption. Here, for modeling purposes, we have approximated the traces shown in Fig. 1c as having constant pressure for a finite amount of time and then increasing linearly until the moment of ignition, see Fig. 4a. Applying this assumption to the five conditions shown in Fig 1c and using SENKIN/VTIM the computed ignition delays show excellent agreement with experimental data as shown in Fig. 4b.

The above results are encouraging and warrant revision of the syngas data of Petersen et al. [8]. It is noted that Petersen et al. [8] did not discuss the characteristics of the pressure signals associated with their shock tube data; however, in recent work [23, 29] they have shown that syngas shock tube ignition can exhibit considerable pressure variations. Furthermore, emission from the hydroxyl radical collected at the shock tube's endwall [23, 29] indicates that these data show severe mild ignition characteristics that, as explained above, in conjunction with boundary layer effects, help compress the test mixture prior to ignition. Since pressure profiles for the data reported by Petersen et al. [8] are not available, Fig. 5 shows results using assumed linear pressure gradients of 2, 5, and 10%/ms prior to ignition. These values are conservative as the presence of mild ignition events will certainly change pressure signals considerably, see Ref. 29. It can be seen that these simplified assumptions yield good agreement with the data over the entire temperature range.

4. Conclusions

High pressure shock tube ignition delays have and continue to be one of the key sources of data that characterize the combustion characteristics of real fuels. At pressures and temperatures of importance to practical applications, concerns have been recently raised as to the

large differences seen between experimental data and chemical-kinetic predictions using the common assumption that the shock tube behaves as a constant volume (V) system with constant internal energy (U). In this paper we have reviewed non-idealities present in shock tubes that can considerably affect the data at extended tests times of several milliseconds needed for the measurement of fuel/air ignition. These effects, coupled with deflagrative processes typical of mild ignition events, serve to compress the test mixture prior to ignition leading to reduced ignition delays. Pre-ignition pressure (and associated temperature) changes have been shown to be reasonably approximated by isentropic assumptions and using well-established kinetic modeling approaches which take into account time-varying systems.

It seems that even though the non-idealities and mild ignition events discussed herein have been known for a long time, their potential importance has not been brought forth sufficiently in the modeling community, and data have not generally been available in the literature that include pressure history during the ignition event. This has led to misinterpretation of data by both experimentalists and kinetic modelers alike. For shock tube studies of fuel/air ignition at high pressures and relatively low temperatures, experimental data must include pressure-time histories. At these conditions it is clear that ignition delay data do not represent pure chemical delay measurements under the ideal conditions of constant pressure and temperature but are affected by phenomena which are facility-specific. This precludes direct cross-comparison of experimental data collected in different venues. These comparisons can only be achieved through modeling.

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References

1. Pfahl, U.; Fieweger, K.; Adomeit, G. *Proc Combust Inst* 1996, 26, 781-789.
2. Fieweger, K.; Blumenthal, R.; Adomeit, G. *Combust Flame* 1997, 109, 599-619.
3. Misawa, S.; Shiraishi, N.; Kosaka, H.; Matsui, Y. *Nihon Kikai Gakkai Nenji Taikai Koen Ronbunshu* 2001, 2, 519-520.
4. Gauthier, B. M.; Davidson, D. F.; Hanson, R. K. *Combust Flame* 2004, 139, 300-311.
5. Davidson, D. F.; Gauthier, B. M.; Hanson, R. K. *Proc Combust Inst* 2005, 30, 1175-1182.
6. Dean, A. J.; Penyazkov, O. G.; Sevruck, K. L.; Varatharajan, B. *Proc Combust Inst* 2007, 31, 2481-2488.
7. Herzler, J.; Fikri, M.; Hitzbleck, K.; Starke, R.; Schulz, C.; Roth, P.; Kalghatgi, G. T. *Combust Flame* 2007, 149, 25-31.
8. Petersen, E. L.; Kalitan, D. M.; Barrett, A. B.; Reehal, S. C.; Mertens, J. D.; Beerer, D. J.; Hack, R. L.; McDonell, V. G. *Combust Flame* 2007, 1-2, 244-247.

9. Fikri, M.; Herzler, J.; Starke, R.; Schulz, C.; Roth, P.; Kalghatgi, G. T. *Combust Flame* 2008, 152, 276-281.
10. Vasu, S. S.; Davidson, D. F.; Hanson, R. K. *Combust Flame* 2008, 152, 125-143.
11. Davidson, D. F.; Haylett, D. R.; Hanson, R. K. *Combust Flame* 2008, in press, doi:10.1016/j.combustflame.2008.01.006
12. Dryer, F. L.; Chaos, M. *Combust Flame* 2008, 152, 293-299.
13. Chaos, M.; Dryer, F. L. *Combust Sci Technol* 2008, 180, 1051-1094.
14. Petersen, E.L.; Hanson, R. K. *Shock Waves* 2001, 10, 405-420.
15. Davidson, D. F.; Hanson, R. K. *Int J Chem Kinet* 2004, 36, 510-523.
16. Kahandawala, M.S.P.; Corera, A.P.; Williams, S.; Carter, C.D.; Sidhu, S.S. *Int J Chem Kinet* 2006, 38, 194-201.
17. Frenklach, M.; Li Kwok Cheong, C. K.; Oran, E. S. *Prog Astronaut Aeronaut* 1984, 95, 722-735.
18. Michael, J. V.; Sutherland, J. W. *Int J Chem Kinet* 1986, 18, 409-436.
19. Blumenthal, R.; Fieweger, K.; Komp, K. H.; Adomeit, G. *Combust Sci Technol* 1996, 113, 137-166.
20. Wang, B. L.; Olivier, H.; Grönig, H. *Combust Flame* 2003, 133, 93-106.
21. Furutani, M.; Kitaguchi, Y.; Yamada, T.; Ohta, Y. *Proc 17th ICDERS, University of Heidelberg, Heidelberg, Germany, July 1999.*
22. Furutani, M.; Ohta, Y.; Kitaguchi, Y.; Osaki, M.; Murai, M.; Isogai, T. *Trans Jpn Soc Mech Eng B* 2001, 67, 2625-2631.
23. Reehal, S. C.; Kalitan, D. M.; Hair, T.; Barrett, A. B.; Petersen, E. L. 5th US Combustion Meeting, San Diego, CA, March 2007, Paper No. C24.

24. Cadman, P.; Thomas, G.O.; Butler, P. *Phys Chem Chem Phys* 2000, 2, 5411-5419.
25. Petersen, E. L.; Lamnaouer, M.; de Vries, J.; Curran, H. J.; Simmie, J.; Fikri, M.; Schulz, C.; Bourque, G. 26th International Symposium on Shock Waves, Göttingen, Germany, July 2007, Paper No. P911.
26. Li, H.; Owens, Z. C.; Davidson, D. F.; Hanson, R. K. *Int J Chem Kinet* 2008, 40, 89-98.
27. Pang, G. A.; Davidson, D. F.; Hanson, R. K. Fall Meeting of the Western States Section of the Combustion Institute, Livermore, CA, October 2007, Paper No. 07F-12.
28. Vasu, S. S.; Davidson, D. F.; Hong, Z.; Vasudevan, V.; Hanson, R. K. *Proc Combust Inst* 32 (2009), in press.
29. Mertens, J. D.; Mussmann, S. S.; Kalitan, D. M.; Petersen, E. L. Spring Meeting of the Western States Section of the Combustion Institute, Los Angeles, CA, March 2008, Paper No. 08S-3.
30. Mittal, G.; Chaos, M.; Sung, C.-J.; Dryer, F. L. *Fuel Process Technol* 2008, in press, doi:10.1016/j.fuproc.2008.05.021.
31. Lutz, E. E.; Kee, R. J.; Miller, J. A. Technical Report SAND87-8248, Sandia National Laboratories, 1987.
32. Kee, R. J.; Rupley, F. M.; Miller, J. A. Technical Report SAND89-8009, Sandia National Laboratories, 1989.
33. Mittal, G.; Sung, C.-J. *Combust Sci Technol* 2007, 179, 497-530.
34. Smith, G. P.; Golden, D. M.; Frenklach, M.; Moriarty, N. W.; Eiteneer, B.; Goldenberg, M.; Bowman, C. T.; Hanson, R. K.; Song, S.; Gardiner, Jr., W.C.; Lissianski, V. V.; Qin, Z.
http://www.me.berkeley.edu/gri_mech/

35. Herbon, J. T.; Hanson, R. K.; Golden, D. M.; Bowman, C. T. *Proc Combust Inst* 2002, 29, 1201-1208.
36. Bates, R. W.; Golden, D. M.; Hanson, R. K.; Bowman, C. T. *Phys Chem Chem Phys* 2001, 3, 2337-2342.
37. Pitz, W. J.; Seiser, R.; Bozzelli, J. W.; Da Costa, I.; Fournet, R.; Billaud, F.; Battin-Leclerc, F.; Seshadri, K.; Westbrook, C. K. Fall Meeting of the Western States Section of the Combustion Institute, Salt Lake City, UT, October 2001, Paper No. 01F-28.
38. Chaos, M.; Zhao, Z.; Kazakov, A.; Gokulakrishnan, P.; Angioletti, M.; Dryer, F. L. 5th US Combustion Meeting, San Diego, CA, March 2007, Paper No. E26.

FIGURE CAPTIONS

Fig. 1. Typical experimental pressure traces during fuel/air ignition in shock tubes; a) data from Fieweger et al. [1]; b) data from Misawa et al. [3]; c) normalized data from Davidson et al. [5]; d) data from Reehal et al. [23].

Fig. 2. Comparison between calculations performed using CHEMSHOCK [26] and SENKIN [31] employing the VTIM option (see text). Predictions with constant U , V assumptions are also shown. Model results are compared with the data of Pang et al. [27]. Both CHEMSHOCK and VTIM approaches use a linear pressure rise of 2%/ms prior to ignition.

Fig. 3. Experimental [5] (symbols) and model [37] predictions (lines, employing constant U , V assumptions) for stoichiometric toluene/air mixtures; the dashed line corresponds to open symbols. Experimental data have been normalized to the pressures shown assuming proportionality to P^{-1} . Pressure traces for data represented by solid symbols can be found in Fig. 1c.

Fig. 4. Effect of pressure rise on the modeling of toluene/air ignition delays; a) pressure profile approximation used as input for SENKIN/VTIM, similar profiles were used for the traces shown in Fig. 1c; b) experimental data and computational results (using the model of Pitz et al. [37]) using constant U , V and including the effect of pre-ignition pressure rise.

Fig. 5. Effect of pre-ignition linear pressure rise applied to the modeling of syngas/air ignition under the conditions of Petersen et al. [8]. Experimental conditions and associated references for the data shown can be found in Refs. 8, 12, 13.

FIGURES

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

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Syngas Chemical Kinetics and Reaction Mechanisms

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Syngas Chemical Kinetics and Reaction Mechanisms

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1. INTRODUCTION

Increasing energy demands domestically and internationally as well as, and perhaps more importantly, in developing countries have resulted in considerable increases and/or fluctuations in energy prices and growing concerns about energy security. These concerns are compounded by environmental issues not only with regard to greenhouse gases, but also the emissions of air pollutants such as nitrogen oxides, sulfur oxides, and mercury. Thus the combustion of “clean” fuels generated from coal, biomass, tar sands, oil shale, and other non-petroleum sources is receiving renewed attention as an option for increasing energy supply and security while reducing environmental impacts. “Syngas” (synthesis gases containing varying amounts of carbon monoxide and hydrogen as the fuel components) derived from these varied resources is expected to play important roles in future power generation and production of liquid hydrocarbon fuel. In the case of power generation, integrated gasification combined cycle (IGCC) power generation based on coal and/or biomass-derived syngas is receiving considerable attention due to the worldwide abundance of coal resources (especially in the U.S., Europe, and Asia). The production of syngas mixtures is also a key approach to generating liquid hydrocarbon fuels through methanol-to-gasoline and distillates (MOGD) (Harandi and Owen, 1990) or Fischer Tropsch (F-T) (Dry, 2002; Wilhelm et al., 2001) conversion. The implementation of carbon capture and storage (Chiesa et al., 2005) has the potential for

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substantially “greening” fossil fuel energy resources, particularly when polygeneration of fuels, chemical products, and electrical power generation are integrated with carbon capture and storage (Larson et al., 2008).

Combustors used in gas turbines operating on syngas and/or hydrogen must be “fuel flexible” as syngas composition can vary greatly, both as a result of the resource(s) from which they are produced, as well as the overall processing environment. Although syngas is mostly composed of hydrogen and carbon monoxide, potential variables to be considered in the direct combustion of syngas mixtures include the carbon/hydrogen ratio, varying levels of carbon dioxide and water, as well as the presence of other trace species that can have a pronounced effect on combustion processes (Glarborg, 2007). Moreover, the flame temperatures of stoichiometric syngas combustion are sufficiently high to result in substantial NO_x emissions. An important aspect of minimizing pollutant emissions from industrial gas turbines operating on natural gas has been the implementation of lean, premixed combustion. A similar approach for turbines operating on syngas and hydrogen is desirable.

Although gasification technologies are well established and syngas combustion is widely used in, for example, refineries for process heat, its application to power generation is not sufficiently developed. In fact, at conditions relevant to industrial turbine mixing systems (i.e. lower temperatures and higher pressures; $T < 1,000\text{ K}$, $10 < P < 30\text{ atm}$), the chemistry and combustion dynamics of syngas as well as hydrogen are not fully understood. This is despite the great amount of detailed studies that have been carried out through the years on the CO/H₂/O₂ kinetic system (e.g. Davis et al., 2005; Dixon-Lewis and Williams, 1977; Gardiner and Olson, 1980; Kim et al., 1994; Li et al., 2007; Rasmussen et al., 2008; Sun et al., 2007; Sung and Law,

2008; Westbrook and Dryer, 1984; Yetter et al., 1991a, 1991b), as this system is the fundamental basis of all hydrocarbon combustion chemistry.

As a result of interest in gas turbine syngas combustion noted above, robust fluid dynamic as well as chemical kinetic modeling tools are sought that are thoroughly validated against experiments spanning a wide range of operating conditions. The ultimate goal of these modeling efforts is to achieve accurate predictive behavior of dynamic combustor features such as blowout, flashback, stability, and autoignition, including how fuel composition might affect these properties (Lieuwen et al., 2008). Driven by the above discussion, data have recently become available (Beerer and McDonell, 2007; Bradley et al., 2007; Burke et al., 2007, 2009a; Kalitan et al., 2006; Mittal et al., 2006; Natarajan et al., 2007; Petersen et al., 2007a; Sivaramakrishnan et al., 2007; Sun et al., 2007; Walton et al., 2007a) for conditions that are sufficiently removed from the range of previous kinetic model validations, as reviewed by Chaos and Dryer (2008). Since this early work and that of Sung and Law (2008), additional experimental data have been published (Beerer and McDonell, 2008; Herzler and Naumann, 2008; Le Cong and Dagaut, 2008; Mertens et al., 2009; Natarajan et al., 2009; Rasmussen et al., 2008) that lend support to further considering the title topic.

A common feature of the studies listed above is the use of undiluted systems (i.e. fuel-air), high pressures and relatively low temperatures in autoignition studies (e.g. Beerer and McDonell, 2008), as well as preheated mixtures in laminar flame speed measurements (e.g. Natarajan et al., 2009). Under these conditions, there have been several reports noting considerable discrepancies between experimental data and kinetic model predictions. These observations motivate further consideration, and it is the purpose of this chapter to discuss the need for careful analysis of data collected at high pressures and the implications that experimental anomalies, known to be

present at these conditions, may have on interpreting these data. This discussion is further motivated by recent evaluations of key reactions in the hydrogen system which will be reviewed below.

This chapter begins with an introduction to the chemistry driving the explosive characteristics of hydrogen oxidation. A review then follows of available chemical kinetic models for simulation of H_2/CO chemistry along with important updates to elementary reactions that can considerably affect the performance of these models at high pressures. Finally, recent experimental ignition and burning velocity data collected at conditions relevant to gas turbine operation are presented and analyzed; emphasis is placed on what implications these data have on further development of new and existing chemical kinetic models. For further overview and background of H_2/CO kinetics, the reader is referred to the work of Chaos and Dryer (2008) and Rasmussen et al. (2008).

2. EXPLOSION CHARACTERISTICS OF H_2 -CONTAINING SYSTEMS

Syngas derived from gasification can consist of high levels of hydrogen depending on the feedstock used. Syngas combustion is very similar in character to that of hydrogen, thus, particularly since the principal reaction producing CO_2 is $CO+OH=CO_2+H$. The reactivity of any fuel-oxidizer mixture is driven by the generation and chain propagation of free active radicals. In the case of carbon monoxide oxidation, in the absence of any source of hydrogen atoms, reactions that can initiate the chain (mainly through propagation of O atoms) are slow at practical conditions, as are reactions of O radicals with CO. The addition of even small amounts of hydrogen or hydrogen-containing species (e.g. water) dramatically increases the rate of CO oxidation (Brokaw, 1967; Yetter et al., 1991a), as radicals are propagated through much faster

hydrogen-related reactions. Hence, in design of syngas combustion systems it is important to have an understanding of the oxidation characteristics of hydrogen as it will determine properties of interest, such as ignition and extinction limits, flame propagation, etc. This is best explained through the concept of explosion limits; i.e. the pressure-temperature boundaries that demarcate regions of slow and explosively fast reaction of a given fuel-oxidizer mixture. Details for hydrogen oxidation explosion limits are given below with emphasis on the conditions of interest in the present study.

Figure 1 shows a typical depiction of the classical explosion limits for hydrogen-oxygen mixtures (Lewis and von Elbe, 1987). These limits arise because of competition between chain-branching and chain-terminating reactions either on surfaces or in the gas phase. Reactions of free radicals with other species yielding more than one free radical as a product would by themselves lead to an exponential growth of the radical pool (i.e. chain-branching reactions). On the other hand, chain propagating reactions only produce one radical for every radical consumed, and reactions that remove radicals entirely can reduce the radical pool. The balance of overall chain propagation with termination processes such that the radical pool neither grows nor decays represents a “critical branching factor” for the chemical reacting system. The critical branching factor for a homogenous gas phase reacting system is a function of system properties, including its temperature, pressure, and reactant mixture fractions. The presence of diffusion and heterogeneous surfaces can also lead to radical production and destruction, modifying the critical branching factor depending on the characteristic time scales of these processes relative to those in the gas phase. Finally, if a reaction is endothermic or exothermic, changes in local temperature as a result of reaction can also affect the critical branching factor. The loci of all

critical branching factor conditions as a function of system parameters define regions of explosive chain branching and slow chemical reaction which are termed explosion limits.

For the following discussion it is assumed that the pressure of a reacting system maintained at a constant temperature of about 750 K is slowly increased from low (< 0.001 atm) to high (> 10 atm) pressures. The reaction properties associated with these constraints, shown in Fig. 1, crosses the explosion limit curve for the hydrogen-oxygen system in three classical explosion limit regimes. The first limit, observed at very low system pressures, is determined by a balance between the removal of radicals on surfaces (wall effect), when diffusion time scales in the gas phase are short in comparison to characteristic reaction time scales. At pressures below the limit, gas phase reaction branching is exceeded by termination (which is dominated by radical diffusion to and termination at surfaces), and the rate of branching is less than the critical branching factor. Above the limit, the rate of radical branching is sufficient to exceed the rate of termination, since there is a greater number of molecular collisions and diffusive time scales increase due to pressure. As the system pressure is further increased, the classical second explosion limit condition is reached, a limit that results entirely from gas phase kinetic processes (i.e. homogeneous gas phase kinetic branching and termination processes). In pure hydrogen oxidation, the most effective chain branching reaction is $\text{H} + \text{O}_2 = \text{O} + \text{OH}$ (R1), while the competing reaction, $\text{H} + \text{O}_2(+\text{M}) = \text{HO}_2(+\text{M})$ (R2), leads to the production of a radical (HO_2) that is much less reactive than OH or O. The time scales for HO_2 to regenerate active radical species at these parameter conditions are very large in comparison to the overall reaction time scale. With increasing pressure, the rate of ternary collisions in reaction (R2) increases relative to binary collisions in (R1). Performing a steady state analysis of the radical pool at the second limit using these two reactions yields the concentration of M (i.e. a collision partner stabilizing reaction R2)

for the classical second limit, given as $[M]=2k_1/k_2$ (Lewis and von Elbe, 1987), where k_i ($i = 1, 2$) represent the specific reaction rate constants of (R1) and (R2) in the forward direction (reverse rates are neglected as they involve processes which are very slow at these condition relative to the forward processes). At higher pressures well above the classical second limit, a third limit condition is reached, as a result of two principal issues: 1) the high concentration of M leads to a sufficient concentration of HO_2 such that reaction $\text{HO}_2+\text{HO}_2=\text{H}_2\text{O}_2+\text{O}_2$ (R3), and subsequent reactions of H_2O_2 , principally $\text{H}_2\text{O}_2(+\text{M})=\text{OH}+\text{OH}(+\text{M})$ (R4), transition the terminating character of (R2) into an overall process (represented by the combination of R2 and the additional subsequent reactions) that is essentially chain propagating; 2) the reaction process becomes very exothermic, and along with increased thermal diffusion timescales with increasing pressure this leads to local mixture self heating (the process is no longer isothermal). Reactions (R2) and (R3) are very exothermic, being moderated by the endothermicity of reaction (R4) (Lee and Hochgreb, 1998).

At high pressures, the character of the reaction also changes with initial reaction temperature. Calculations shown in Fig. 2a exemplify this behavior. These computations were performed for a constant volume, adiabatic, and stoichiometric H_2/O_2 system at an initial pressure of 20 atm and for temperatures of 1000 K and 1300 K; these conditions are also marked in Fig. 1. The displayed results are normalized in each case by the initial temperature and by the time at which the maximum rate of temperature rise is observed. At 1000 K, a significant increase in the system temperature is seen during a chemical induction period due to heat release associated with the above reactions (R2, R3, R4), while at 1300 K, no similar heat release effect is observed. Also shown in Fig. 2b is a plot of characteristic reaction times (determined by the ratio of the initial H_2 concentration to the maximum H_2 consumption rate) as a function of

temperature for the same system. Figure 2b shows that as temperature increases there is a distinct transition in characteristic reaction times indicating the presence of an “explosion limit.” Increasing temperatures produces an increasing flux of HO₂ radicals via HO₂+H₂=H₂O₂+H (R5), generating H radicals. H radicals, in turn, react with the abundant HO₂ through HO₂+H=H₂+O₂ (R6) and HO₂+H=OH+OH (R7). Reaction (R6) is chain terminating whereas (R7) is chain branching. Therefore, a system which is initially straight-chain in overall reaction character (i.e. R2→R3→R4) can become chain branching as a result of temperature rise (R2→R5→R7,R4). The limit observed under these conditions is an extension of the classical second limit, modified by the importance of added termination and branching routes (R6 and R7) at high pressures and temperatures. A steady state analysis of the radical pool considering these additional reactions leads to the determination of a critical third body concentration (i.e. pressure) marking the explosion limit as

$$[M] = \frac{k_1}{k_2 \left(\frac{1}{1 + \frac{k_7}{k_6}} \right)}$$

This limit is typically referred to as the “extended” second limit (Mueller et al., 1996; Mueller et al., 1999a). The relevance of the extended second limit to overall system behavior depends upon a comparison of chemical kinetic time scales with convective, back mixing, and/or diffusive time scales (Mueller et al., 1996; Mueller et al., 1999a; Zheng and Law, 2004).

Figure 2b shows that at temperatures below the extended second limit the overall reaction is characterized by a high activation energy. Thus any self-heating that occurs during induction (see Fig. 2a), is important to overall system behavior. Conditions located in the region between the third limit and the extended second limit can be described as leading to thermal-chain

explosions (Fig. 1), where heat release from slow chain propagating reactions brings a reactive mixture to a chain-branched explosive condition, as explained above. This region, for example, is associated with mild ignition phenomena observed in shock tubes (Strehlow and Cohen, 1962; Meyer and Oppenheim, 1970; Oppenheim, 1985), as will be further detailed below. On the other hand, at pressures below and temperatures above the extended second limit, explosions are non-thermal and strictly due to chain-branching, characterized by relatively low overall activation energies (see Fig. 2b).

For conditions relevant to practical syngas applications (e.g. lean premixed gas turbine engines), typical pressures are on the order of 30 atm and temperatures not in excess of 1000 K. These conditions place these systems in the thermal-chain explosion regime. Therefore, chemical kinetics defining the extended second limit remain an important aspect in the design of such combustion systems. In fact, the recent experimental studies listed above have placed new emphasis on the importance of the chemistry of the hydroperoxyl radical (HO_2) as well as hydrogen peroxide (H_2O_2) due to the conditions studied. These investigations are the subject of further analyses given below.

3. RECENT AND PROPOSED UPDATES TO THE H_2/CO KINETIC MODEL

Kinetic models that can be applied to hydrogen and syngas systems continue to be refined (Davis et al., 2005; Konnov, 2008; Li et al., 2004, 2007; O’Connaire et al., 2004; Rasmussen et al., 2008; Sun et al., 2007; Wang et al. 2007) as new rate evaluations, thermochemical parameters with reduced uncertainties, and experimental validation data become available. For example, Li et al. (2004, 2007) recently revised prior work by updating the detailed H_2/O_2 model of Mueller et al. (1999a). The updates by Li et al. included a revision in the rate correlations

used for the branching reaction (R1), taken from Hessler (1998), and for the low pressure of the competing reaction (R2), adopted from Michael et al. (2002). A major constraint in selecting these two correlations was that their ratio in the temperature range between 800K and 900K replicated the ratio experimentally determined by Mueller et al. (1998). This ratio is a representation of the critical third body concentration (i.e. pressure) that marks the classical second explosion limit ($[M]=2k_1/k_2$), as described above. In fact, as models develop, one has to ensure that they can properly represent the classical explosion limits of the hydrogen system; such tests, however, often are not performed. Figure 3 shows comparisons of explosion limit data against predictions from the kinetic models listed above (Davis et al., 2005; Konnov, 2008; Li et al., 2004, 2007; Sun et al., 2007). Agreement is good overall but some differences are appreciable. For example, at 0.1 atm the models predict a range of temperatures for transition into the explosive regime of about 745 to 765 K. These differences manifest when using the models to predict observables such as ignition delay at conditions near the extended second limit (see such computations using various models, including Li et al., 2004 and O’Connaire et al., 2004, can be found in the recent works of Konnov, 2008 and Ströhle and Myhrvold, 2007).

Experimental measurements and theoretical studies continue to appear in the literature for both (R1) and (R2) (Bates et al., 2001; Fernandes et al., 2008; Hahn et al., 2004; Hwang et al., 2005; Sellevåg et al., 2008; Troe, 2000; Troe and Ushakov, 2001) to further reduce uncertainties in predicted rates, particularly at temperatures below 1000 K. For example, Fig. 4 compares recent correlations for the low pressure rate of reaction (R2) with N₂ as the collisional partner. Although some uncertainties remain, (e.g. see Hwang et al., 2005), all of them lie within 20% of each other and within the uncertainty estimates derived from the literature review of Baulch et al. (2005). Figure 5 shows calculations for the effective rate of (R2) using values obtained from the

recent work of Fernandes et al. (2008) and Sellevåg et al. (2008). Overall, values differ by about 25% over the temperature and pressure range of interest to practical applications. Fernandes et al. (2008) claim these differences are due to a less complete database and a less detailed analysis considered by Sellevåg et al. (2008).

Nevertheless, studies of (R2) remain important especially in determining the collisional efficiencies of species such as water and carbon dioxide. Efficiencies are hard to determine experimentally and associated uncertainties can be considerable; furthermore, the interaction of polar species such as water in (R2) is not completely understood (Michael et al., 2002). The presence of these species increases the recombination rate of (R2), effectively shifting the explosion limit behavior of H_2/O_2 . The explosion limit data shown in Fig. 3 was adjusted to make all values relative to N_2 . However, for comparison, model results are also plotted for a mixture consisting of 10% (mol) H_2O . The presence of this highly effective collision partner has a very noticeable impact; pressure and temperature conditions for which a N_2 system is explosive (e.g. 1 atm and 950 K) can become non-explosive with the addition of water. This has direct implications in practical systems where back-mixing of reaction products in combustor recirculation zones (for example, to control NO_x emissions) can change combustion behavior and stability.

Other reactions of critical importance in the oxidation of $\text{H}_2/\text{CO}/\text{O}_2$ as well as moist CO mixtures have received further attention recently. Li et al. (2007) employed a weighted empirical fit of the entire body of experimentally measured rate constants for reactions $\text{CO}+\text{OH}=\text{CO}_2+\text{H}$ (R8), $\text{HCO}+\text{M}=\text{H}+\text{CO}+\text{M}$ (R9), and $\text{HCO}+\text{O}_2=\text{HO}_2+\text{CO}$ (R10); all of which have strong impact on the burning rate of hydrocarbon flames (Zhao et al., 2005).

New high pressure data (described above) have allowed analyses to be performed that have lead to proposed updates in some of the reactions involving HO_2 , two of the most significant being the rate correlations for $\text{CO} + \text{HO}_2 = \text{CO}_2 + \text{OH}$ (R11) and $\text{HO}_2 + \text{OH} = \text{H}_2\text{O} + \text{O}_2$ (R12). Mittal et al. (2006, 2007) used data from high pressure rapid compression machine (RCM) ignition of $\text{H}_2/\text{CO}/\text{O}_2/\text{N}_2/\text{Ar}$ mixtures and noted that rate of (R11) could be up to a factor of ten lower than some accepted values (e.g. Baulch et al., 1973). This is consistent with the recommendation of Mueller et al. (1999b), who argued, based on flow reactor data, that lower values for (R11) might be justified upon further evaluation. Theoretically, (R11) has received less attention in comparison to other reactions in the CO/hydrogen system (Allen et al., 1996; Sun et al., 2007; You et al., 2007). The detailed treatment of You et al. (2007) (which considered critical geometries, hindered internal rotations, as well as the complex potential energy surface of R10) supports a much lower rate for (R11) than those commonly used in kinetic models. Chaos and Dryer (2008) showed that implementing the rate of You et al. (2007) in the model of Li et al. (2007) considerably improved predictions against the data of Mittal et al. (2006), see Fig. 6. Chaos and Dryer (2008) and Li et al. (2007) also showed through computational singular perturbation analyses (CSP) (Kazakov et al., 2006) how reaction (R11) contributed to the ignition process through its effect on the induction period. Chaos and Dryer (2008) further concluded that the updates put forth by Mittal et al. (2006) and You et al. (2007) for (R10) can be readily absorbed into current kinetic models without affecting the quality of their predictions against validation targets that are insensitive to induction chemistry[†].

Reaction (R12) is of particular significance in oxygen rich systems; for example, (R12) can alter the nature of the extended second limit as the relative importance of O and OH radicals

[†] Li et al. now distribute their 2007 model with the substitution of the parameters of You et al. (2007) for those of Mueller et al. (1999a).

as chain carriers varies with the presence of excess oxygen. Reaction (R12) has been mostly studied at atmospheric conditions (Braun et al., 1982; Burrows et al., 1981; Cox et al., 1981; DeMore, 1979, 1982; Goodings and Hayhurst, 1988; Keyser, 1988; Kurylo et al., 1981; Lii et al., 1980; Peters and Mahnen, 1973; Rozenshtein et al., 1984; Sridharan et al., 1984) due to the significance of this reaction in the HO_x cycle of atmospheric chemistry. More recently, high temperature measurements (Hippler et al. 1995; Kappel et al., 2002) have shown that (R12) exhibits an uncommon and highly non-Arrhenius behavior, indicative of the formation of an activated complex (see Fig. 7). Sivaramakrishnan et al. (2007) identified (R12) as a sensitive reaction in studying oxidation of H₂/CO/O₂/Ar mixtures in a high-pressure shock tube (up to 450 atm). They parameterized reaction (R12) by fitting experimental data and capturing the unusually narrow and deep minimum in the rate at about 1000-1200 K. However, the fit gives larger weight to the data of Hippler et al. (1995) rather than to the more recent, and arguably more reliable, measurements of Kappel et al. (2002), Fig. 7. The expression thus derived was able to improve predictions (using the model of Davis et al., 2005) against the data of Sivaramakrishnan et al. (2007).

Chaos and Dryer (2008) noted that the expression proposed by Sivaramakrishnan et al. (2007) could reach values over the collision limit at temperatures greater than about 1400 K. They performed least squares analyses by considering the data of Srinivisan et al. (2006) and Goodings and Hayhurst (1988) who showed very little temperature dependence of the rate for (R12) for temperatures greater than about 1300 K. Two fits were performed taking into account the two different minima observed by Hippler et al. (1995) and Kappel et al. (2002). The resulting expressions are plotted in Fig. 7.

Li et al. (2007) performed CSP analyses of model results under the conditions of Sivaramakrishnan et al. (2007). Chaos and Dryer (2008) further extended these analyses to show that over the temperature range of interest (1200 – 1400K) for the study of Sivaramakrishnan et al. (2007), the data only support the likelihood of a lower rate for reaction (R12). As pressure increases, reaction (R12) strongly competes with (R7) for HO₂ radicals. Reaction (R7) is one of the major direct sources of OH at high pressures (especially near the extended second limit), thus determining the amount of OH available to react with CO through (R8). Therefore, reactions involving HO₂ that compete for and generate OH radicals (such as reactions R7 and R12) become more important at high pressures in the H₂/CO system since the availability of OH determines the rate of CO oxidation. Sivaramakrishnan et al. (2007) noted that their data could be reconciled by increasing the rate of (R11), which is consistent with the above argument, as (R11) both consumes CO and releases OH; however increasing this rate degrades model predictions against flow reactor data (Kim et al., 1994) and, as discussed above, recent studies support a much lower rate for (R11). The update proposed by Sivaramakrishnan et al. (2007) as well as by Chaos and Dryer (2008) essentially lowers the rate of (R12) over the temperature range of interest (see Fig. 5), thus slowing a termination path for both HO₂ and OH. At higher pressures (> 250 atm), (R12) is not as sensitive (Chaos and Dryer, 2008) since the flux of HO₂ to form H₂O₂ through (R3) is considerably larger than through reaction (R12) and, at high temperatures, H₂O₂ decomposes rapidly to yield OH (R4), removing the significance of reaction (R12).

Clearly, additional studies of (R12) are required; the lack of experimental data at intermediate temperatures (400-900 K), however, makes finding an expression that accurately captures the observed temperature dependence challenging. Moreover, reactions (R6) and (R7)

continue to have large uncertainties associated with their rates and temperature dependences, which, as shown above, can have a direct effect in the determination of the oxidation characteristics of systems near the extended second limit.

4. HIGH-PRESSURE/LOW-TEMPERATURE SYNGAS IGNITION AND KINETIC IMPLICATIONS

Ignition of H_2/CO mixtures has traditionally been studied at relatively low pressures and high temperatures (e.g. Dean et al., 1978). These conditions correspond to the chain-branched or strong ignition regime shown in Fig. 1. The need to establish an experimental database at conditions found in practical applications has recently led to considerable interest in syngas ignition at high pressures and relatively low temperatures. Perhaps the most representative of such studies is that of Petersen et al. (2007a) who reported new ignition delay data for syngas/air mixtures in a shock tube and a flow reactor. These new data are summarized here in Fig. 8 along with other recently published data from the rapid compression study of Walton et al (2007a) and from an earlier high pressure flow reactor study described by Peschke and Spadaccini (1985). All of the ignition delay data have been normalized to conditions of 20 atm pressure. Petersen et al. (2007a) noted that at reaction temperatures lower than about 1050 K, experimental observations of ignition delay, although consistent among the different apparatuses considered, all begin to differ considerably from kinetic model predictions generated using homogeneous, zero-dimensional, isochoric assumptions (i.e. constant internal energy, U , and volume, V) typically employed by kineticists, see Fig. 8.

The above discussion raises considerable concern as these results bring into question the predominant fundamental kinetic understanding of gas phase oxidation phenomena for the H_2/CO system. Hydrogen and carbon monoxide oxidation are the fundamental basis for all

hydrocarbon combustion chemistry and severe deficiencies in reaction rates and/or thermochemistry sufficient to be the cause of these disparities would be far reaching. Yet, the noted discrepancies between syngas ignition delay experimental results and gas phase kinetic predictions are repeatable and real and, thus, they impose limitations to design of lean premixed gas turbine systems using syngas and/or hydrogen.

As noted in section 2 above, carbon monoxide oxidation is strongly influenced by the presence of small amounts of hydrogen-containing species, including moisture, hydrocarbons, and, most importantly, hydrogen itself (e.g. Yetter et al., 1991a). Subsequently, ignition phenomena for syngas/air mixtures will be similar in character to those for hydrogen/air mixtures. In fact, hydrogen shock tube ignition delay results exhibit similar disparities between predictions and observations and have been frequently discussed in the published literature since the early 1960s. This has been detailed by Chaos and Dryer (2008) and is shown in Fig. 9. Note the remarkable similarity between Fig. 9 and results reported by Petersen et al. (2007a) for syngas (Fig. 8).

In considering the observations above, Dryer and Chaos (2008) and Chaos and Dryer (2008) emphasized that the high sensitivity of induction chemistry to any type of experimental perturbations or non-idealities is what principally led to similarities in observations amongst the various experimental venues. Furthermore they argued that disparities in observations and kinetic predictions were a result of the ideal modeling assumptions applied and their inability to represent experimental conditions appropriately. In the particular case of shock tube observations, the disparities occur at temperatures below the extended second explosion limit where mild ignition occurs (Strehlow and Cohen, 1962) and characteristic kinetic times are

strongly influenced by induction chemistry and heat release involving HO_2 and H_2O_2 reactions, see section 2.

Since the publication of the study of Chaos and Dryer (2008), several papers have drawn attention to the fact that significant pressure variations can occur during ignition in shock tubes at long test times (several milliseconds or longer). These revelations have significant impact on the arguments made with regard to syngas combustion as well as model validation based upon shock tube data presently in the literature. Below, further attention is brought to these issues, along with their implications in interpreting and modeling ignition delay data.

Shock tube pressure histories

Shock-induced self-ignition of undiluted fuel/air mixtures at the conditions of interest noted above are characterized by relatively long ignition delay times on the order of a few milliseconds. Ignition under these conditions is strongly coupled to the thermodynamic state and fluid dynamics of the gas behind the reflected shock wave. Ideally, the gas behind a reflected shock should be stationary and have uniform thermodynamic properties over the entire test volume. In the case of syngas/air mixtures, ideal analyses further predict that no significant pre-ignition heat release can occur without substantial depletion of reactants, voiding the philosophical definition of “ignition.”

Practically, however, even for dilute mixture studies, unavoidable non-idealities exist in the shocked gases, due to the ubiquitous presence of boundary layers. Incident shock attenuation, boundary layer growth, and shock-wave/boundary-layer interactions lead to non-uniform pressures and temperatures behind the reflected shock which gradually increase with time (Davidson and Hanson, 2004; Kahandawala et al., 2006; Petersen and Hanson, 2001).

Furthermore, residual gas velocities may exist behind the reflected shock wave which further lead to the establishment of pressure gradients along the shock tube axis (Frenklach et al., 1984; Michael and Sutherland, 1986). These non-idealities can be minimized by using large-diameter shock tubes, dilute fuel/oxidizer mixtures in monoatomic gases, and short test times (less than about 500 μ s). The latter two options, however, are not applicable to shock tube experiments that study higher concentration fuel/air mixtures of direct relevance to energy conversion applications.

For such highly reactive, exothermic mixtures, the above phenomena are further compounded by the fact that at high pressures and lower temperatures, ignition in reflected shock tube regions is inhomogeneous (Terao, 1977), initiating at localized “hot spots” in a deflagrative manner, progressing eventually to detonation (Blumenthal et al., 1996; Fieweger et al., 1997; Wang et al., 2003). An example of this behavior is shown in Fig. 10, which contrasts ignition processes during mild and strong combustion. Prior to the main ignition event, the finite exothermicity of the initial, localized, heterogeneous reaction sites induces further increases in pressure which are quickly equalized throughout the gases behind the reflected shock due to the high speed of sound. These features are typical of the well-known mild ignition process. For non-reactive mixtures, Petersen and Hanson (2001) reported temperature increases (due to observed pressure gradients behind the reflected shock) of up to 40 K over 500 μ s for representative pressure and temperature ranges of 24-530 atm and 1275-1900 K, respectively. For conditions relevant to practical fuels (i.e. 25-50 atm and 700-1000 K) and due to reactivity and the likelihood of much longer ignition times, more severe pressure and temperature effects are to be expected. It should be noted, however, that the magnitude of these changes also depend

on the shock tube diameter (Petersen and Hanson, 2001), being less severe (but still considerable) as the tube diameter is increased.

From the discussion above, it is clear that changes in the thermodynamic state of the gas behind the reflected shock wave are likely to be significant and, thus, can have pronounced effects on kinetic observations as well as the ignition process. Figure 11 shows the pressure-time history record during ignition of a sample syngas mixture studied by Reehal et al. (2007). A pre-ignition pressure increase of nearly 50% over the reported nominal reflected shock pressure can be observed (Fig. 9b). In such instances, kinetic modeling of the ignition delay process as a under the common assumption that the shock tube behaves as a constant volume system with constant internal energy is no longer reasonable. Approximate homogenous modeling can be performed if individual experimental pressure histories are known for each test condition; however, this information rarely accompanies reported shock tube ignition delay measurements. With some frequency an exemplar experimental pressure profile is presented, but generally the ordinate scaling chosen (large enough to capture pre- and post-ignition pressure values) is such that pressure history prior to ignition is not known with sufficient accuracy. (Fig. 11a).

Even though the aforementioned non-idealities present in shock tubes at the conditions of interest have been known for some time and noted by shock tube experimentalists (e.g. Blumenthal et al., 1996; Fieweger et al., 1997; Petersen and Hanson, 2001), recent shock tube studies of fuel/air mixtures have failed to consider these phenomena in interpreting the reported data (e.g. Petersen et al., 2007a). Furthermore, because of the lack of pressure-time history information noted above and the established, common practice to assume constant U , V in modeling shock tube data, the experimental and general chemical kinetic modeling communities (including ourselves) have ignored the implications to model validation.

The issues outlined above have recently begun to receive more attention, as shock tube experimentalists continue to understand and attempt to determine early ignition events at lower temperatures and for high energy density mixtures (Li et al., 2008; Pang et al., 2009; Petersen et al., 2007b; Shen et al., 2009). In these studies ignition delay data are further examined and pressure variations prior to ignition are identified and taken into account when interpreting and modeling the data. Their implications into how ignition delay chemical kinetic modeling should be approached are discussed below.

Modeling Approaches

In several previous studies, it has been suggested that pre-ignition pressure variations in reflected shock tube observations can be approximated by assuming they are polytropic processes (Fieweger et al., 1997; Petersen and Hanson, 2001). Recently, some investigators (e.g. Pang et al., 2009) have used pressure histories and associated temperatures deduced from isentropic relations to adjust ignition data affected by pre-ignition pressure rise, while others (e.g. Petersen et al., 2007b) have opted to compute an effective or average pressure and temperature based on the observed pressure history and plot the data with respect to these adjusted values. The presence of dynamic pressure features prior to ignition, however, can have considerable effects on radical initiation processes, as discussed in Mittal et al. (2008). Therefore it is important to include measured pressure histories in modeling approaches rather than using averaged or effective values

Li et al. (2008) proposed a specific modeling tool for shock tube applications, CHEMSHOCK, which allows for the treatment of time-varying pressures coupled with chemical kinetics. CHEMSHOCK solves the coupled energy and chemical species system of differential

equations using a two-step process: at every time step the system is first solved assuming constant U , V conditions, and then pressure and temperature are adjusted isentropically to match the measured pressure profile while keeping the chemical composition fixed. Pang et al. (2009) showed promising results using CHEMSHOCK in modeling ignition delay data of H_2/O_2 mixtures.

Alternatively, SENKIN (Lutz et al., 1987), part of the CHEMKIN-II (Kee et al., 1989) suite of programs, is capable of embodying the same assumptions with similar generality. A time-dependent polytropic compression (or expansion) results in both volume and density changing with time. In contrast to the CONP (constant enthalpy and pressure) and CONV (constant internal energy and volume, commonly used for shock tube modeling), the VTIM (i.e. volume as a function of time) option in SENKIN can be employed to emulate a time-dependent polytropic state change. The user must only provide time functions for variations in the specific volume of the system. Knowing the functional variation of pressure from measured data and assuming isentropic compression/expansion, the functions to be provided are:

$$\nu(t) = \frac{1}{\rho_0} \left[\frac{P(t)}{P_0} \right]^{-1/\gamma}$$

$$\frac{d\nu}{dt} = -\frac{1}{\gamma} \frac{\nu(t)}{P(t)} \frac{dP}{dt}$$

where ν is the specific volume, P the measured pressure, γ the specific heat ratio, and P_0 and ρ_0 are the initial pressure and density, respectively, behind the reflected shock wave. This approach has been successfully used in modeling rapid compression machine ignition processes (Mittal et al., 2008), while Petersen and Hanson (2001) used a similar methodology to account for observed pressure variations in non-reacting mixtures behind reflected shock waves.

Using this approach, the syngas data of Reehal et al. (2007) was further considered. It was assumed that pre-ignition pressure rise, on average, can be approximated by a linear positive gradient, as evidenced by Pang et al., 2009. It is noted, however, that for high reactant concentrations (i.e. fuel/air mixtures) and due to the mild ignition processes discussed above, observed pressure rises may deviate from this linearity (e.g. see Fig. 2 in Petersen et al., 2007b). As shown in Fig. 11b, an approximate rise of 6 atm/ms can be applied to the data. Figure 12 plots the dataset for the mixture shown in Fig. 11 along with model predictions using a constant U, V assumption as well as VTIM with the pressure rise shown in Fig. 11b. For the shortest test time, the constant U, V model predictions agree reasonably with the data, but at longer test times, the gradual pressure (and temperature) increase results in considerable departure of predictions and measurements, as noted above. In this case, Fig. 12 shows that the constant U, V approach quickly fails to provide a good estimate of ignition delay at lower temperatures. SENKIN modeling with VTIM assuming a linear pressure profile provides much improved predictions.

The above results are encouraging and warrant consideration in interpreting the syngas data of Petersen et al. (2007a). It is noted that Petersen et al. (2007a) did not discuss the characteristics of the pressure signals associated with their shock tube data; however, in recent work (Mertens et al. 2008; Reehal et al., 2007) these researchers have shown that syngas shock tube ignition can exhibit considerable pressure variations. Furthermore, emission from the hydroxyl radical collected at the shock tube's endwall (Reehal et al., 2007) indicates that these data show severe mild ignition characteristics that, as explained above, in conjunction with boundary layer effects lead to compression of the test mixture over the ignition delay period. In fact, Fig. 8 also shows shock tube data from the H_2 /air ignition study of Blumenthal et al. (1995) who were able to identify and perform temporal measurements on the appearance of flame

kernels and subsequent transition to detonation in the mild ignition regime. Cases which exhibited mild ignition processes are identified in Fig. 8 as open circles; note that these closely agree with the shock tube data from Petersen et al. (2007a) which considerably deviate from constant U , V model predictions. Since pressure profiles for the data reported by Petersen et al. (2007a) are not available, Fig. 8 shows results using assumed linear pressure gradients of 2, 5, and 10%/ms (i.e. 0.4, 1, and 2 atm/ms) prior to ignition. These values may be conservative as the presence of mild ignition events will certainly change pressure signals considerably; for example, Fig. 11b shows a pressure gradient of nearly 50%/ms. It can be seen that these simplified assumptions yield good agreement with the data over the entire temperature range. However, the accuracy of the measured pressure histories in the pre-ignition region as well as the validity of the isentropic compression assumption produce additional uncertainties that must be considered in developing validating models utilizing such data.

Other systems

One of the more intriguing points raised by data in Fig. 8 is that data collected in flow reactor and rapid compression venues apparently follow the trend established by the shock tube data in the mild ignition regime. Given that non-idealities present in shock tubes (discussed above) do not apply to these experiments, the question remains as to what causes accelerated ignition in these systems. Chaos and Dryer (2008) suggested that both flow reactors and rapid compression measurements can suffer similarly from other experimental perturbations. The strong sensitivity of chemical induction processes in the thermal-chain explosive regime to any source of perturbation lead to reductions in the overall ignition delay period in the mild ignition region (see Fig. 8) similar to those observed for shock tube studies.. The presence of reaction

fronts (Walton et al., 2007b) as well as particles (Elsworth et al., 1969; Haskell, 1970) may influence rapid compression studies. On the other hand, catalytic processes may affect flow reactor measurements (Chaos and Dryer, 2008). All these perturbations act to remove the rate limiting nature of reactions such as (R4) and (R5) increasing the exothermicity of the system during induction rapidly driving the reaction across the explosion limit, considerably shortening induction and, therefore, ignition delay time.

The multiplicity of and the strong sensitivities of induction chemistry to experimental perturbations are very difficult to characterize accurately in research experiments and are unlikely to be controlled in real engineering applications. The implications for developing lean premixing schemes for advanced syngas gas turbine applications are that designs should accommodate the likely presence of perturbations and their effects on ignition delay through, for example, empirical relations (Beerer and McDonell, 2008), if stimulated flashback into the mixing region is to be precluded.

5. PREMIXED FLAME PROPAGATION IN HIGH PRESSURE MEDIA

One parameter of great importance in the design of gas turbine combustors using syngas and/or hydrogen is the laminar burning velocity, and, in turn, the turbulent mass burning rate. Measurements of syngas burning velocities have been mostly studied at atmospheric conditions (e.g. Hassan et al., 1996; McLean et al., 1994). A number of recent advancements in flame speed measurement methodologies have resulted in a substantial extension in the range of initial parameters and mixture compositions that can be studied. Tse et al. (2000) devised a constant-pressure dual-chambered cylindrical bomb apparatus, extending the pressure range for the stretched spherical flame method by nearly an order of magnitude. The device enabled H_2 and

H₂/CO flame speed measurements up to 40 atm (Tse et al. 2000, Sun et al. 2007). Bradley et al. (2007) conceived a method to extract planar burning velocities from wrinkled outwardly-propagating flames and employed the technique to measure burning velocities of lean H₂-air flames up to 10 atm. Natarajan et al. (2007) demonstrated that the Bunsen flame approach for flame speed measurement yields values that are consistent with other, more widely accepted methodologies. Flame speeds were determined using conical H₂/CO/CO₂/He flames at pressures to 15 atm and preheat temperatures to 700K (Natarajan 2007, 2009).

In a study of transient effects arising from ignition in a homogeneous mixture, Chen et al. (2009a) found that unsteady and nonlinear effects are substantial for small, spherical flames of non-unity Lewis number. Burke et al. (2009b) and Chen et al. (2009b) showed that flame speeds observed close to the wall in cylindrical and spherical chambers are systematically lower due to confinement of the flow field. Correction techniques were developed that extend the flame radius range that can be used for accurate determinations of flame speed allowing for burning velocity measurements of dilute mixtures with prolonged ignition transients. The techniques of Burke et al. (2009b) and Chen et al. (2009a, 2009b) permitted experimental study on the burning rates of H₂/O₂/CO/CO₂/diluent flames of flame temperatures from 1500 to 1800K in a cylindrical bomb up to 25 atm (Burke et al., 2007, 2009a). Similar to the recent ignition delay observations discussed in the previous section, the above flame speed studies extend results significantly beyond previous works with which modeling results presently in the literature were compared. Furthermore, it appears that current kinetic models result in predictions that fail to replicate these recent data, see Fig. 13.

Figure 13 shows that there exists considerable scatter in available atmospheric pressure measurements (Fig. 13a) (Burke et al., 2007; Hassan et al., 1997; McLean et al., 1994; Sun et al.,

2007), especially at rich conditions. A similar trend is also observed for high pressure H_2/CO flame conditions (Fig. 13b) (Burke et al., 2009a; Sun et al., 2007). Inconsistencies that may be present in data processing methodologies to obtain laminar burning velocities (e.g. Burke et al., 2007, 2009b; Chen et al., 2009b) cannot fully explain the observed disparities. Sun et al. (2007) noted these discrepancies and developed a syngas kinetic model that exhibited improved predictions against high pressure H_2/CO flames. Sun et al. also demonstrated acceptable model performance against other H_2/CO targets (Dean et al., 1978; Fotache et al., 2000; Mueller et al., 1999b; Yetter et al., 1991b). However, as shown in Fig. 14, model updates implemented by Sun et al. (2007) seriously degrade the quality of predictions against high pressure pure hydrogen burning velocities.

On the basis of the above discussion, Chaos and Dryer (2008) considered the possibility of experimental contamination effects due to unintentional addition of iron pentacarbonyl, $Fe(CO)_5$. For laboratory combustion experiments, many researchers have employed high pressure carbon-steel cylinders as the source of the fuel. CO can readily react at high pressure with metals present in steel to form carbonyls; especially $Fe(CO)_5$. Depending on handling, steel CO cylinders obtained from commercial suppliers with, initially, little or no contaminants are prone to contamination by $Fe(CO)_5$ over time (Tepe et al., 1999). An example of experimental contamination by $Fe(CO)_5$ is the study of Williams and Shaddix (2007) who recently reported observing wall deposits formed when operating a swirl-stabilized combustor running on simulated syngas-air mixtures; these deposits were found to be mostly iron oxides originating from $Fe(CO)_5$ in the CO source used.

Metallic compounds have been shown to have strong flame inhibition effects (Lask and Wagner, 1960; Linteris et al., 2008; Reinelt and Linteris, 1996; Rumminger and Linteris, 2000,

2002; Rumminger et al., 1999; Vanpee and Shirodkar, 1978). When present in premixed flames, iron pentacarbonyl can reduce the burning velocity considerably (Lask and Wagner, 1960; Linteris et al., 2008; Reinelt and Linteris, 1996; Rumminger and Linteris, 2000). The presence of chromium, nickel, and iron carbonyls have also been shown to accelerate carbon monoxide and hydrogen oxidation in shock tubes (Izod et al., 1972; Linteris and Babushok, 2009; Matsuda, 1972a; Matsuda, 1972b). For the conditions of the study of Petersen et al. (2007a), however, the presence of $\text{Fe}(\text{CO})_5$ is not sufficient (Chaos and Dryer, 2008; Linteris and Babushok, 2009) to explain the results discussed in the section above. Finally, in gas turbines used in commercial IGCC installations, the formation of large iron deposits on nozzle hardware has been noted. These deposits lead to restriction/alteration of the airflow into the combustor, overheating parts of the combustion chamber. These iron deposits have been reported to originate from $\text{Fe}(\text{CO})_5$ introduced into the chamber after CO in the syngas used reacted with steel pipes (García, 2006). Furthermore, iron pentacarbonyl is a well-established challenge in the development of gasification technologies (Rezaiyan and Cheremisinoff, 2005). Other contaminants generated during feedstock gasification that can considerably alter combustion chemistry include nitrogen and sulfur oxides (Chaos and Dryer, 2008; Mueller et al., 1999b; Mueller et al., 2000).

To further investigate the effects of $\text{Fe}(\text{CO})_5$ contamination on H_2/CO burning velocities, Chaos and Dryer (2008) added the $\text{Fe}(\text{CO})_5$ kinetic rate correlations and transport properties developed by Rumminger et al. (1999) to the model of Li et al. (2007) and performed calculations for the flame conditions of Fig. 13. In the computations, it was assumed that the CO source contained 200 ppm of $\text{Fe}(\text{CO})_5$ so that the overall maximum iron pentacarbonyl mixture concentrations for a wide range of equivalence ratios were always less than 75 ppm, approximately. Figure 13 compares the model-predicted burning velocities for pure fuel (solid

lines) and for mixtures using CO contaminated by 200 ppm of $\text{Fe}(\text{CO})_5$ (dashed lines) with experimental data. The figure confirms that $\text{Fe}(\text{CO})_5$ has a very noticeable effect on rich flames, in qualitative agreement with the onset of the experimental disparities found in the literature.

Experimental data, however, is needed to conclusively determine contamination by iron pentacarbonyl. As part of the present study, the CO cylinder used in the experiments of Burke et al. (2007) was analyzed by Fourier Transform Infrared Spectroscopy means. A Nicolet Magna IR 560 spectrometer was used for the tests. The instrument consisted of a 2.0 liter gas cell with an optical path length of 10.0 meters maintained at 100°C and 0.07 atm (~ 1 psia). Rather than trying to handle $\text{Fe}(\text{CO})_5$ (due to its high toxicity) to perform a calibration, pure CO was obtained from Airgas, stored in an aluminum cylinder to prevent formation of iron pentacarbonyl. The gas from this cylinder was used to establish a background signal. Absorption spectra from the CO gas stored in the steel cylinder used by Burke et al. (2007) was then recorded by averaging thirty-two scans at a resolution of 0.25 cm^{-1} over a 600 to 4000 cm^{-1} wavenumber range.

The results of the tests are shown in Fig. 15; the typical rovibrational CO band heads (R and P branches) do not appear in the spectra as pure, $\text{Fe}(\text{CO})_5$ -free carbon monoxide was used as background. However, strong absorption bands are evident, centered around 2013 and 2033 cm^{-1} . These are positioned at relatively higher frequencies than the CO rovibrational frequencies and can be ascribed to the presence of gas phase $\text{Fe}(\text{CO})_5$ (McDowell, 1971; Myrstad and Fredriksen, 1998; Rao et al., 1989) as it only has two CO stretching modes which are IR active (Rao et al., 1989). Based on the absorbance values measured and using the extinction coefficients reported by McDowell (1971) for the 2013 and 2033 cm^{-1} bands, consistent concentration values of 25.7 and 24.3 ppm, respectively, were calculated. This contamination level is approximately an order

of magnitude lower than that used to generate the plots in Fig. 13. Therefore, the data of Burke et al. (2007) can be considered free from iron pentacarbonyl effects.

The discussion above motivated additional consideration of the important kinetic pathways affecting the propagation of flames at high pressure, particularly for diluted and low flame temperature conditions. Such conditions are of considerable significance as combustion dilution is essential to controlling NO_x emissions in syngas combustion applications. Burke et al. (2009a) performed experimental and modeling studies of H₂/CO/CO₂ flames of flame temperatures from 1500 to 1800K at high pressures. Significant disagreement among the model predictions as well as with experimental data were noted to correlate strongly with high pressure, and lower flame temperature conditions where the reactive portion of the flame was restricted to a smaller, higher temperature window. The discrepancies were found to exist even for pure hydrogen flames.

Preliminary experimental data from Burke et al. (2009a) and model predictions (Li et al. 2007, Davis et al. 2005, Sun et al. 2007, Konnov 2008) for the mass burning rate of both lean and rich H₂/O₂/diluent mixtures are shown in Fig. 16. The experimental data show a negative pressure dependence of the burning rate for pressures above ~15 atm for these low flame temperature conditions. Negative pressure dependence of the burning rate for syngas flames could have interesting consequences for thermo-acoustic stability behavior in engines. While the predictions of Li et al. (2007) and Davis et al. (2005) reproduce experimental results well to about 10 atm, no model reproduces the new measurements for pressures above 10 atm across all equivalence ratios. Large disparities in predicted burning rates at higher pressures (up to factor of 2) are observed among the models and against the experimental data. The disparity in

predictions yielded from the various models is particularly noteworthy, as nearly the same target data were used in developing and validating each of the models.

Analyses conducted using the model of Li et al. (2007) indicate that sensitivity of mass burning rate predictions to elementary rates increases considerably with pressure, as demonstrated in Fig. 17. The reactions, to which the pressure dependence for rich conditions is most sensitive, are primarily reactions that involve H atoms, namely (R1), (R2), (R6), and (R7) (Fig. 17b). Rates of these four reactions define the extended second explosion limit, as discussed above. The reactions that appear to govern the pressure dependence for lean conditions are the reactions above in addition to reactions involving OH radicals, namely (R12) and $\text{H}_2 + \text{OH} = \text{H}_2\text{O} + \text{O}$ (R13) (Fig. 17a). Other reactions include $\text{O} + \text{H}_2 = \text{H} + \text{OH}$ (R14) and $\text{H} + \text{OH} + \text{M} = \text{H}_2\text{O} + \text{M}$ (R15). Reaction (R14) is a branching reaction that becomes increasingly important at lean conditions, as more O radicals are produced due to the presence of excess oxygen. Even at lean conditions, however, reaction (R1) is the dominant branching reaction (Fig. 17). Reaction (R15) is highly exothermic and has been previously shown to affect predictions of laminar burning rates (Li et al., 2004); in fact Li et al. (2004) modified the rate of (R15) to improve model predictions at flame conditions. Uncertainties in collision parameters of species stabilizing the recombination of H and OH in (R15) remain and have been the subject of recent studies (Sellevåg et al., 2008; Srinivasan and Michael, 2006). At increasing pressures, the OH radical is present in higher concentrations and plays a larger role in the kinetic pathways for lean conditions. Reaction (R12) competes with (R6) and (R7) for HO_2 radicals and inhibits the overall kinetics by converting two radicals to stable species. As discussed above, the reaction rate of (R12) has an uncommon and highly non-Arrhenius temperature dependence (see Fig. 7). Temperature window sensitivity analyses (Zhao et al. 2005) of burning rate to (R12) for the lean

$\text{H}_2/\text{O}_2/\text{He}$ mixture of Fig. 16a were conducted (Burke et al., 2009a). The results (shown in Fig. 18) reveal that the temperature window of peak sensitivity to (R12) at pressures above 10 atm is almost exclusively in the deep “well” of the rate correlation (around 1000K, see Fig. 7). Therefore, accurate characterization of the rate of (R12) in this region is critical to predicting the burning rate of lean syngas mixtures at pressures of practical significance. Indeed, simulations performed using the model of Li et al. (2007) substituting the two rate expressions proposed by Chaos and Dryer (2008) for (R12) yield substantially different results at pressures above 10 atm. Substitution of the fit based on the data of Hippler et al. (1995), which exhibits a local minimum at $\sim 1200\text{K}$, yields substantially higher values than those shown in Fig. 16, whereas substitution of the fit based on the Kappel et al. (2002), which exhibits a local minimum at $\sim 1000\text{K}$, has little effect on the predictions. Additionally, direct substitution of recent rate expressions for (R2) and (R15) proposed by Srinivasan & Michael (2006), Sellevåg et al. (2008), and Pang et al. (2009) into the mechanism of Li et al. (2007) do not substantially improve, and in some cases degrade, predictions. Direct substitution of the proposed rate expression from Michael et al. (2000) for (R6) yields improvements to the predictions, but does not completely reconcile differences between the models and experimental data. At present it appears that under fuel rich conditions, the relative rates of $\text{HO}_2 + \text{H} = \text{H}_2 + \text{O}_2$ (R6) and $\text{HO}_2 + \text{OH} = \text{OH} + \text{OH}$ (R7) must be significantly revised to bring predictions into reasonable consistency with experimental results. As these reactions remain important even under fuel lean conditions, further refinements of predictions involving $\text{HO}_2 + \text{OH} = \text{H}_2\text{O} + \text{O}_2$ (R12) are dependent on them. Additional experimental and theoretical analyses on Reactions R6, R7, and R12 are needed to support resolution of models at conditions important to syngas combustion at high pressures.

The effect of pressure on the flame structure based on flux of H radicals through the competing pathways, (R1) and (R2), and H radical mole fraction using the model of Li et al. (2007) is illustrated in Fig. 19 (Burke et al., 2009a). Figure 19 also shows the temperature of the extended second limit for the given pressures (see also Fig. 1). The results indicate that with increasing pressure, the temperature of extended second limit increases accordingly, moving significantly toward the post-flame region for lean and rich mixtures. Therefore, the portion of the flame that undergoes strong branching kinetics (i.e. at temperatures above the extended second limit) is reduced to a smaller temperature window at higher pressures. The peak H radical mole fraction is decreased substantially and also moves toward the post-flame region with increasing pressure. Furthermore, the reaction zone region in which (R1) and (R2) compete is restricted to higher temperatures and a smaller overall temperature range as pressure is increased. Similar shifts toward smaller, higher temperature windows occur in the flux profiles of other controlling reactions, including (R6) and (R7). Such a restriction of the strongly reactive portion of the flame to higher temperatures can be expressed as an increase in the overall activation energy or Zeldovich number of the mixture with pressure.

Comparing Figs. 19a and 19b, the responses of the flame structure to pressure are different for different equivalence ratios. The peak fluxes of the H radical through (R1) and (R2) occur closer to the unburned region in rich flames, where the concentration of oxygen is higher. Since the peak flux of the H radical occurs at lower temperatures, where (R2) is favored relative to (R1), the peak flux through (R2) relative to (R1) is higher compared to lean conditions. At both lean and rich conditions, the mole fraction of HO_2 compared to H is substantially higher at higher pressures as a much larger portion of the flame is below the extended second limit. Consequently, pathways involving HO_2 play a much larger role in the overall kinetics. Reactions

involving HO_2 with H and OH (and possibly even O for very lean conditions) exhibit higher sensitivities to the burning rate at higher pressures. Additionally, since the reactive portion of the flame is restricted to higher temperatures at high pressures, the peak sensitivity to these reactions occurs at higher temperatures (e.g. see Fig. 18). Since (R6), (R7), and (R12) continue to have large uncertainties in their rates and temperature dependences as discussed above, these reactions deserve further attention, particularly at higher temperatures (above 1000 K).

In general, high pressure syngas as well as hydrogen flames emphasize HO_2 kinetics and radical-radical recombination reactions such as (R15). Additionally, most of the flame reactivity i.e. branching) occurs in a relatively small portion of the flame as for increasing pressures the extended second limit shifts to higher temperatures. Since many new techniques have been developed in the past decade that extend the pressure and temperature ranges of flame studies and recent interest in syngas combustion is focused on conditions relevant to gas turbines, further investigations of high pressure and temperature syngas flame kinetics are surely forthcoming. As many of the recent studies (Tse et al., 2000; Sun et al., 2007; Natarajan et al., 2009; Burke et al., 2009a) have motivated changes to the models or highlight model discrepancies with experimental data, substantial improvements in modeling flames at gas turbine conditions will likely occur over the next decade.

6. CONCLUSION

Syngas mixtures are an increasingly important commodity in developing low polluting, solutions to energy security and resources in a carbon-constrained world. Interest in gas turbine syngas combustion has inspired an extension of the existing experimental validation resources to considerably higher pressures and lower temperatures that are sufficient for testing the

comprehensive nature of existing detailed chemical kinetic models. The present chapter has considered some of the unique properties of syngas combustion kinetics, summarized a number of recent theoretical and experimental advancements on the fundamental understanding of important elementary reactions, reviewed new experimental efforts to provide validation data for high pressure, high energy density kinetic behavior, and discussed the kinetic issues that relate to improving predictions of these new data. The higher pressure, lower temperature conditions encountered in gas turbines points to the importance and the need of further theoretical as well as experimental studies of elementary reactions involving HO_2 and H_2O_2 . We note that recent re-evaluations of the reaction rate for $\text{CO} + \text{HO}_2 = \text{CO}_2 + \text{OH}$ (R11) are primarily important to ignition delay measurements at high pressures due to modifications of induction chemistry and have little influence on post induction observations. It appears that modifications in the reaction of $\text{HO}_2 + \text{OH} = \text{H}_2\text{O} + \text{O}_2$ (R12) improve comparisons of predictions with high pressure oxidation, but recommended rate correlations for this reaction should be modified to avoid exceeding collisional rates at high temperatures.

We show that recent investigations of high pressure ignition and flame propagation of H_2/CO mixtures should be cautiously evaluated prior to implementing any changes to improve the agreement of predictions from chemical kinetic models. H_2/CO ignition measurements in shock tubes, rapid compression machines, and flow reactors can exhibit aberrations at low temperature and high pressures that cause observations to considerably differ from homogenous gas phase predictions. Although phenomena characterized as mild ignition in hydrogen-oxygen shock tube experiments are historically well known and can even be kinetically differentiated from strong ignition observations, the source(s) of chemical induction perturbations that lead to their manifestation are not understood in quantitative detail. Behavior of syngas mixtures under

similar conditions is derived almost entirely as a result of perturbations of hydrogen-oxygen chemical induction kinetics, with only minor differences from the presence of carbon monoxide. Numerous processes can affect induction chemistry (i.e. compressible flow, physical mixing, and/or catalytic surface coupling), and it is likely that even in shock tubes, no one cause is universally responsible for the mild ignition observations. Moreover, that multiple sources of chemical induction perturbations can all lead to similar magnitudes of reduction in ignition delay in the mild ignition regime is the reason that observations in shock tube venues can be “correlated” with experimental observations in other venues (flow reactors, rapid compression machine experiments). However, it is unlikely that in real systems, the multiple sources of perturbations can be controlled to an extent such that homogenous kinetic predictions provide limiting, realistic design criteria. While the exact nature and relative importance of each perturbing source in the various experimental venues remains to be determined, simple engineering approximations can be valuable for the safe design of lean premixing systems for gas turbines, based upon fundamental experimental data.

Carbon monoxide stored in high-pressure carbon-steel cylinders is commonly used in laboratory research. These sources are prone to contamination by metal carbonyls and it has been shown through computations that these contaminants, especially iron pentacarbonyl, can considerably affect fuel rich H_2/CO laminar burning velocities. The potential effect of this contaminant in applied conditions is relatively unknown, but it is important that fuel-rich burning rate measurements used for validation of kinetic models should be carefully scrutinized for contaminant effects.

Finally, we note that all of the hydrogen-oxygen kinetic models in the literature are deficient in yielding predictions of laminar burning rates at all equivalence ratios, pressures and

flame temperatures of likely importance to gas turbine applications. While the key reactions that most affect burning rates under these conditions are identified, a suitable solution, supported by fundamental kinetic results remains to be achieved. Additional fundamental work on the reaction of HO₂ with OH and H radicals, as well as characterizations of H₂O₂ and these radicals under reaction conditions would be extremely beneficial in further constraining model validation at high pressures and temperatures.

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REFERENCES

- Allen, T.L., Fink, W.H., and Volman, D.H. (1996) Theoretical Studies of the Mechanism of the Gas Phase Reaction of the Hydroperoxo Radical with Carbon Monoxide to Form Hydroxyl Radical and Carbon Dioxide. *J. Phys. Chem.*, 100, 5299-5302.
- Baldwin, R.R., Jackson, D., Walker, R.W., and Webster, S.J. (1967) Interpretation of the Slow Reaction and Second Limit of Hydrogen Oxygen Mixtures by Computer Methods. *T. Faraday Soc.*, 63, 1676-1686.
- Bates, R.W., Golden, D.M., Hanson, R.K., and Bowman, C.T. (2001) Experimental study and modeling of the reaction $H + O_2 + M \rightarrow HO_2$ ($M = Ar, N_2, H_2O$) at elevated pressures and temperatures between 1050 and 1250 K. *Phys. Chem. Chem. Phys.*, 3, 2337-2342.
- Baulch, D.L., Bowman, C.T., Cobos, C.J., Cox, R.A., Just, T., Kerr, J.A., Pilling, M.J., Stocker, D., Troe, J., Tsang, W., and Walker, R.W. (2005) Evaluated Kinetic Data for Combustion Modeling: Supplement II. *J. Phys. Chem. Ref. Data*, 34, 757-1397.
- Baulch, D.L., Drysdale, D.D., Duxbury, J., and Grant, S. (1973) *Evaluated Kinetic Data for High Temperature Reactions*. Vol. 3, Butterworths, London.
- Baulch, D.L., Griffiths, J.F., Pappin, A.J., and Sykes, A.F. (1988) Stationary-State and Oscillatory Combustion of Hydrogen in a Well-Stirred Flow Reactor. *Combust. Flame*, 73, 163-185.
- Beerer, D.J. and McDonell, V.G. (2007) Experimental Study of Ignition Delay for Application to Hydrogen and Syn-gas Fired Lean Premixed Gas Turbine Engines. *Proceedings of the Fifth U.S. Combustion Meeting*, San Diego, CA, paper E01.

- Beerer, D.J. and McDonell, V.G. (2008) Autoignition of Hydrogen and Air inside a Continuous Flow Reactor with Application to Lean Premixed Combustion. *J. Eng. Gas Turbines Power*, 130, 051507.
- Blumenthal, R., Fieweger, K., Komp, K.H., Adomeit, G., and Gelfand B.E. (1995) Self-Ignition of H₂-Air Mixtures at High Pressure and Low Temperature. *Proc. of the 20th Int. Symp. on Shock Waves*, 935-940.
- Blumenthal, R., Fieweger, K., Komp, K.H., and Adomeit, G. (1996) Gas Dynamic Features of Self Ignition of Non Diluted Fuel/Air Mixtures at High Pressure. *Comb. Sci. Tech.*, 113-114, 137-166.
- Bradley, D., Lawes, M., Liu, K., Verhelst, S., and Woolley, R. (2007) Laminar Burning Velocities of Lean Hydrogen–Air Mixtures at Pressures up to 1.0 MPa. *Combust. Flame*, 149, 162-172.
- Braun M., Hofzumahaus, A., and Stuhl F. (1982) VUV Flash-Photolysis Study of the Reaction of HO with HO₂ at 1 Atm and 298 K. *Ber. Bunsenges. Phys. Chem.*, 86, 597-602.
- Brokaw, R.S. (1967) Ignition Kinetics of the Carbon Monoxide-Oxygen Reaction. *Proc. Combust. Inst.*, 11, 1063-1073.
- Burke, M.P, Chaos, M., Dryer, F.L., and Ju, Y. (2009a) The Dependence of Mass Burning Rates of H₂/CO/CO₂ Flames on Pressure and Flame Temperature, to appear.
- Burke, M.P., Chen, Z., Ju, Y., and Dryer, F.L. (2009b) Effect of Cylindrical Confinement on the Determination of Laminar Flame Speeds Using Outwardly Propagating Flames, *Combust. Flame*, accepted for publication.

- Burke, M.P., Qin, X., Ju, Y., and Dryer, F.L. (2007) Measurements of Hydrogen Syngas Flame Speeds at Elevated Pressures. *Proceedings of the Fifth U.S. Combustion Meeting*, San Diego, CA, paper A16.
- Burrows, J.P., Cox, R.A., and Derwent, R.G. (1981) Modulated Photolysis of the Ozone-Water Vapour System: Kinetics of the Reaction of OH with HO₂. *J. Photochem.*, 16, 147-168.
- Chaos, M. and Dryer, F.L. (2008) Syngas Combustion Kinetics and Applications. *Combust. Sci. Tech.*, 180, 1051–1094.
- Chen, Z., Burke, M.P., and Ju, Y. (2009a) Effects of Lewis Number and Ignition Energy on the Determination of Laminar Flame Speed Using Propagating Spherical Flames. *Proc. Combust. Inst.*, 32, in press, doi:10.1016/j.proci.2008.05.060.
- Chen, Z., Burke, M.P., and Ju, Y. (2009b) Effects of Compression and Stretch on the Determination of Laminar Flame Speed Using Propagating Spherical Flames, *Combust. Theor. Model.*, accepted for publication.
- Chiesa, P., Consonni, S., Kreutz, T., and Williams R.H. (2005) Co-production of Hydrogen, Electricity and CO₂ from Coal with Commercially Ready Technology. Part A: Performance and Emissions. *Int. J. Hydrogen Energ.*, 30, 747-767.
- Cox, R.A., Burrows, J.P., and Wallington, T.J. (1981) Rate Coefficient for the Reaction OH + HO₂ = H₂O + O₂ at 1 Atmosphere Pressure and 308 K. *Chem. Phys. Lett.*, 84, 217-221.
- Craig, R.R. (1966) A Shock Tube Study of the Ignition Delay of Hydrogen-Air Mixtures Near the Second Explosion Limit. Report AFAPL-TR-66-74, Air Force Aeropropulsion Lab, Wright-Patterson.
- Davidson, D.F. and Hanson, R.K. (2004) Interpreting Shock Tube Ignition Data. *Int. J. Chem. Kinet.*, 36, 510-523.

- Davis, S.G., Joshi, A.V., Wang, H., and Egolfopoulos, F. (2005) An Optimized Kinetic Model of H_2/CO Combustion. *Proc. Combust. Inst.*, 30, 1283-1292.
- Dean, A.M., Steiner, D.C., and Wang, E.E. (1978) A Shock Tube Study of the $\text{H}_2/\text{O}_2/\text{CO}/\text{Ar}$ and $\text{H}_2/\text{N}_2\text{O}/\text{CO}/\text{Ar}$ Systems: Measurement of the Rate Constant for $\text{H} + \text{N}_2\text{O} = \text{N}_2 + \text{OH}$. *Combust. Flame*, 32, 73-84.
- DeMore, W.B. (1979) Reaction of HO_2 with O_3 and the Effect of Water Vapor on HO_2 Kinetics. *J. Phys. Chem.*, 83, 1113-1118.
- DeMore, W.B. (1982) Rate Constant and Possible Pressure Dependence of the Reaction Hydroxyl + Hydroperoxo. *J. Phys. Chem.*, 86, 121-126.
- Dixon-Lewis, G. and Williams, D.J. (1977) The Oxidation of Hydrogen and Carbon Monoxide. In Branford, C.H. and Tipper, C.F.H. (eds.) *Comprehensive Chemical Kinetics*, Elsevier, Amsterdam, vol. 17, pp. 1-248.
- Dry, M.E. (2002) The Fischer-Tropsch Process: 1950-2000. *Catal. Today*, 71, 227-241.
- Dryer, F.L. and Chaos, M. (2008) Ignition of Syngas/Air and Hydrogen/Air Mixtures at Low Temperatures and High Pressures: Experimental Data Interpretation and Kinetic Modeling Implications. *Combust. Flame*, 152, 293-299.
- Egerton, A. and Warren, D.R. (1951) Kinetics of the Hydrogen/Oxygen Reaction. I. The Explosion Region in Boric Acid-Coated Vessels. *Proc. Roy. Soc. A – Math. Phys.*, 204, 465-476.
- Elsworth, J.E., Haskell, W.W., and Read, I.A. (1969) Non-Uniform Ignition Processes in Rapid-Compression Machines. *Combust. Flame*, 13, 437-438.
- Fernandes, R.X., Luther, K., Troe, J., and Ushakov, V.G. (2008) Experimental and Modelling Study of the Recombination Reaction $\text{H} + \text{O}_2 (+\text{M}) \rightarrow \text{HO}_2 (+\text{M})$ between 300 and 900 K,

- 1.5 and 950 bar, and in the Bath Gases $M = \text{He, Ar, and N}_2$. *Phys. Chem. Chem. Phys.*, 10, 4313-4321.
- Fieweger, K., Blumenthal, R., and Adomeit, G. (1997) Self-Ignition of S.I. Engine Model Fuels: A Shock Tube Investigation at High Pressure. *Combust. Flame*, 109, 599-619.
- Fotache, C.G., Tan, Y., Sung, C.-J., and Law, C.K. (2000) Ignition of $\text{CO/H}_2/\text{N}_2$ versus Heated Air in Counterflow: Experimental and Modeling Results. *Combust. Flame*, 120, 417-426.
- Frenklach, M., Li Kwok Cheong, C.K., and Oran, E. S. (1984) LDV Measurements of Gas Flow behind Reflected Shocks. *Prog. Astronaut. Aeronaut.*, 95, 722-735.
- Fujimoto, S. (1963) Chemical Reaction In A Shock Wave I: The Ignition Delay of a Hydrogen-Oxygen Mixture in a Shock Tube. *Bull. Chem. Soc. Japan*, 36, 1233-1236.
- García, F. (2006) Syngas Combustion Experience at the Puertollano IGCC Plant. *ASME Turbo Expo 2006*, panel discussion GT2006-91352.
- Gardiner, Jr., W.C. and Olson, D.B. (1980) Chemical Kinetics of High Temperature Combustion. *Ann. Rev. Phys. Chem.*, 31, 377-399.
- Glarborg, P. (2007) Hidden Interactions - Trace Species Governing Combustion and Emissions. *Proc. Combust. Inst.*, 31, 77-98.
- Goodings, J.M. and Hayhurst, A.N. (1988) Heat Release and Radical Recombination in Premixed Fuel-Lean Flames of $\text{H}_2 + \text{O}_2 + \text{N}_2$ - Rate Constants for $\text{H} + \text{OH} + \text{M} = \text{H}_2\text{O} + \text{M}$ And $\text{HO}_2 + \text{OH} = \text{H}_2\text{O} + \text{O}_2$. *J. Chem. Soc. Faraday Trans. 2*, 84, 745-762.
- Hahn, J., Krasnoperov, L., Luther, K., and Troe, J. (2004) Pressure Dependence of the Reaction $\text{H} + \text{O}_2 (+\text{Ar}) = \text{HO}_2 (+\text{Ar})$ in the Range 1-900 bar and 300-700 K. *Phys. Chem. Chem. Phys.*, 6, 1997-1999.

- Harandi, M.N. and Owen, H. (1990) Integrated staged conversion of methanol to gasoline and distillate. United States Patent 4899002.
- Haskell, W.W. (1970) Fuel Ignition in a Rapid Compression Machine: Sensitivity to Flame Ignition by Particles. SAE Paper 700059.
- Hassan, M.I., Aung, K.T., Faeth, G.M. (1996) Markstein Numbers and Unstretched Laminar Burning Velocities of Wet Carbon Monoxide Flames. AIAA Paper 96-0912.
- Herzler, J. and Naumann, C. (2008) Shock Tube Study of the Ignition of Lean CO/H₂ Fuel Blends at Intermediate Temperatures and High Pressure. *Combust. Sci. Tech.*, 180, 2015-2028.
- Hessler, J.P. (1998) Calculation of Reactive Cross Sections and Microcanonical Rates from Kinetic and Thermochemical Data. *J. Phys. Chem. A*, 102, 4517-4526.
- Hippler, H. and Troe, J. (1992) Rate Constants of the Reaction HO + H₂O₂ → HO₂ + H₂O at T (1000 K. *Chem. Phys. Lett.*, 192, 333-337
- Hippler, H., Neubauer, H., and Troe, J. (1995) Shock Wave Studies of the Reactions HO + H₂O₂ (H₂O + HO₂ and HO + HO₂ (H₂O + O₂ between 930 and 1680 K. *J. Chem. Phys.*, 103, 3510-3516.
- Hippler, H., Troe, J., and Willner, J. (1990) Shock Wave Study of the Reaction HO₂ + HO₂ → H₂O₂ + O₂: Confirmation of a Rate Constant Minimum near 700 K. *J. Chem. Phys.*, 93, 1755-1760.
- Hwang S.M., Ryu, S.-O., De Witt, K.J., and Rabinowitz, M.J. (2005) High Temperature Rate Coefficient Measurements of H + O₂ Chain-Branching and Chain-Terminating Reaction. *Chem. Phys. Lett.*, 408, 107-111.

- Izod, T.P.J, Kistiakowsky, G.B., and Matsuda, S. (1972) Mechanism of Oxidation of Carbon Monoxide in the Presence of Chromium Carbonyl. *J. Chem. Phys.*, 56, 1083-1090.
- Kahandawala, M.S.P., Corera, A.P., Williams, S., Carter, C.D., and Sidhu, S.S. (2006) Investigation of Kinetics of Iso-Octane Ignition under Scramjet Conditions. *Int. J. Chem. Kinet.*, 38, 194-201.
- Kalitan, D.M., Petersen, E.L., Mertens, J.D., and Crofton, M.W. (2006) Ignition of Lean CO/H₂/Air Mixtures at Elevated Pressures. ASME Paper GT2006-90488.
- Kappel, Ch., Luther, K., and Troe, J. (2002) Shock Wave Study of the Unimolecular Dissociation of H₂O₂ in its Falloff Range and of its Secondary Reactions. *Phys. Chem. Chem. Phys.*, 4, 4392-4398.
- Kazakov, A., Chaos, M., Zhao, Z., and Dryer, F.L. (2006) Computational Singular Perturbation Analysis of Two-Stage Ignition of Large Hydrocarbons. *J. Phys. Chem. A*, 110, 7003-7009.
- Kee, R.J., Rupley, F.M., and Miller, J.A. (1989) CHEMKIN II: A Fortran Chemical Kinetics Package for the Analysis of Gas Phase Chemical Kinetics. Technical Report SAND89-8009, Sandia National Laboratories.
- Keyser, L.F. (1988) Kinetics of the Reaction OH + HO₂ (H₂O + O₂ From 254 K to 382 K. *J. Phys. Chem.*, 92, 1193-1200.
- Kim, T.J., Yetter, R.A., and Dryer, F.L. (1994) New Results on Moist CO Oxidation: High Pressure, High Temperature Experiments and Comprehensive Kinetic Modeling. *Proc. Combust. Inst.*, 25, 759-766.
- Konnov, A.A. (2008) Remaining Uncertainties in the Kinetic System of Hydrogen Combustion. *Combust. Flame*, 152, 507-528.

- Kurylo, M.J., Klais, O., and Laufer, A.H. (1981) Mechanistic Investigation of the $\text{HO} + \text{HO}_2$ Reaction. *J. Phys. Chem.*, 85, 3674-3678.
- Larson, E.D., Fiorese, G., Liu, G., Williams, R.H., Kreutz, T.J., and Consonni, S. (2008) Co-production of Synfuels and Electricity from Coal + Biomass with Zero Net Carbon Emissions: an Illinois Case Study. *Energy Procedia*, in press.
- Lask, G. and Wagner, H.Gg. (1960) Influence of Additives on the Velocity of Laminar Flames. *Proc. Combust. Inst.*, 8, 432-438.
- Le Cong, T. and Dagaut, P. (2008) Experimental and Detailed Kinetic Modeling of the Oxidation of Methane and Methane/Syngas Mixtures and Effect of Carbon Dioxide Addition. *Combust. Sci. Tech.*, 180, 2046-2091.
- Lee, D. and Hochgreb, S. (1998) Hydrogen Autoignition at Pressures above the Second Explosion Limit (0.6–4.0 MPa). *Int. J. Chem. Kinet.*, 30, 385-406.
- Lewis, B. and von Elbe, G. (1987) *Combustion, Flames and Explosion of Gases*. 3rd Ed., Academic Press, Inc., Orlando.
- Li, H., Owens, Z.C., Davidson, D.F., and Hanson, R.K. (2008) A Simple Reactive Gasdynamic Model for the Computation of Gas Temperature and Species Concentrations behind Reflected Shock Waves. *Int. J. Chem. Kinet.*, 40, 89-98.
- Li, J., Zhao, Z., Kazakov, A., and Dryer, F.L. (2004) An Updated Comprehensive Kinetic Model of Hydrogen Combustion. *Int. J. Chem. Kinet.*, 36, 566-575.
- Li, J., Zhao, Z., Kazakov, A., Chaos, M., Dryer, F.L., and Scire, Jr., J.J. (2007) A Comprehensive Kinetic Mechanism for CO , CH_2O , and CH_3OH Combustion. *Int. J. Chem. Kinet.*, 39, 109-136.

- Lieuwen, T., McDonell, V.G., Petersen, E.L., and Santavicca, D. (2008) Fuel Flexibility Influences on Premixed Combustor Blowout, Flashback, Autoignition, and Stability. *J. Eng. Gas Turbines Power*, 130, 011506.
- Lii, R.-R., Corse, R.A., Sauer, M.C., and Gordon, S. (1980) Temperature Dependence of the Gas-Phase Self-Reaction of Hydroperoxo Radicals In The Presence Of Ammonia. *J. Phys. Chem.*, 84, 813-817.
- Linteris, G.T. and Babushok, V.I. (2009) Promotion or Inhibition of Hydrogen-Air Ignition by Iron-Containing Compounds. *Proc. Combust. Inst.*, 32, in press, doi:10.1016/j.proci.2008.09.006.
- Linteris, G.T., Rumminger, M.D., and Babushok V.I. (2008) Catalytic Inhibition of Laminar Flames by Transition Metal Compounds. *Prog. Energ. Combust. Sci.*, 34, 288-329.
- Lutz, A.E., Kee, R.J., and Miller, J.A. (1987) SENKIN: A Fortran Program for Predicting Homogeneous Gas Phase Chemical Kinetics with Sensitivity Analysis. Technical Report SAND87-8248, Sandia National Laboratories.
- Martynenko, V.V., Penyaz'kov, O.G., Ragotner, K.A., and Shabunya, S.I. (2004) High-Temperature Ignition of Hydrogen and Air at High Pressures Downstream of the Reflected Shock Wave. *J. Eng. Phys. Thermophys.*, 77, 785-793.
- Matsuda, S. (1972a) Gas Phase Homogeneous Catalysis in Shock Waves. II. The Oxidation of Carbon Monoxide by Oxygen in the Presence of Iron Pentacarbonyl. *J. Chem. Phys.*, 57, 807-812.
- Matsuda, S. (1972b) Gas Phase Homogeneous Catalysis in Shock Waves. III. The Oxidation of Carbon Monoxide by Oxygen in the Presence of Nickel Carbonyl. *J. Phys. Chem.*, 76, 2833-2838.

- McDowell, R.S. (1971) Metal Carbonyl Vapors: Rapid Quantitative Analysis by Infrared Spectrophotometry. *Amer. Ind. Hyg. Ass. J.*, 32, 621-624.
- McLean, I.C., Smith, D.B., and Taylor, S.C. (1994) The Use of Carbon Monoxide/Hydrogen Burning Velocities to Examine the Rate of the CO + OH Reaction. *Proc. Combust. Inst.*, 25, 749-757.
- Mertens, J.D., Kalitan, D.M., Barrett, A.B., and Petersen, E.L. (2009) Determination of the Rate of $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$ ($\text{M} = \text{N}_2, \text{Ar}, \text{H}_2\text{O}$) from Ignition of Syngas at Practical Conditions. *Proc. Combust. Inst.* 32, in press, doi:10.1016/j.proci.2008.06.163.
- Mertens, J.D., Musmann, S.S., Kalitan, D.M., and Petersen, E.L. (2008) A Chemical Kinetics Model for the Fast Ignition of Syngas at Lower Temperatures and Higher Pressures. *Spring Meeting of the Western States Section of the Combustion Institute*, Los Angeles, CA, March 2008, Paper No. 08S-3.
- Meyer, J.W. and Oppenheim, A.K. (1970) On the Shock Induced Ignition of Explosive Gases. *Proc. Combust. Symp.*, 13, 1153-1164.
- Michael, J.V. and Sutherland, J.W. (1986) The Thermodynamic State of the Hot Gas behind Reflected Shock Waves: Implications to Chemical Kinetics. *Int. J. Chem. Kinet.*, 18, 409-436.
- Michael, J.V., Su, M.C., Sutherland, J.W., Carroll, J.J., and Wagner, A.F. (2002) Rate Constants for $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$ in Seven Bath Gases. *J. Phys. Chem. A*, 106, 5297-5313.
- Michael, J.V., Sutherland, J.W., Harding, L.B., and Wagner, A.F. (2000) Initiation in H_2/O_2 : Rate Constants for $\text{H}_2 + \text{O}_2 \rightarrow \text{H} + \text{HO}_2$ at High Temperature. *Proc. Combust. Inst.*, 28, 1471-1478.

- Mittal, G., Chaos, M., Sung, C.-J., and Dryer, F.L. (2008) Dimethyl Ether Autoignition in a Rapid Compression Machine: Experiments and Chemical Kinetic Modeling. *Fuel. Process. Technol.*, 89, 1244-1254.
- Mittal, G., Sung, C.-J., and Yetter, R.A. (2006) Autoignition of H₂/CO at Elevated Pressures in a Rapid Compression Machine. *Int. J. Chem. Kinet.*, 38, 516–529.
- Mittal, G., Sung, C.-J., Fairweather, M., Tomlin, A.S., Griffiths, J.F., and Hughes, K.J. (2007) Significance of the HO₂+CO Reaction during the Combustion of CO+H₂ Mixtures at High Pressures. *Proc. Combust. Inst.*, 31, 419-428.
- Mueller, M.A., Yetter, R.A., and Dryer, F.L. (1996) Explosion Limit Behavior of Dilute Hydrogen-Oxygen Mixtures from 0.3 to 3.0 atm and 850 to 950 K. *Fall Meeting of the Eastern States Section of the Combustion Institute*, Hilton Head Island, SC, December 1996.
- Mueller, M.A., Kim, T.J., Yetter, R.A., and Dryer, F.L. (1999a) Flow Reactor Studies and Kinetic Modeling of the H₂/O₂ Reaction. *Int. J. Chem. Kinet.*, 31, 113-125.
- Mueller, M.A., Yetter, R.A., and Dryer, F.L. (1999b) Flow reactor studies and kinetic modeling of the H₂/O₂/NO_x and CO/H₂O/O₂/NO_x reactions. *Int. J. Chem. Kinet.*, 31, 705-724.
- Mueller, M.A., Yetter, R.A., and Dryer, F.L. (1998) Measurement of the Rate Constant for H + O₂ + M (HO₂ + M (M = N₂, Ar) Using Kinetic Modeling of the High-Pressure H₂/O₂/NO_x Reaction. *Proc. Combust. Inst.*, 27, 177-184.
- Mueller, M.A., Yetter, R.A., and Dryer, F.L. (2000) Kinetic Modeling of the CO/H₂O/O₂/NO/SO₂ system: Implications for High-Pressure Fall-Off in the SO₂ + O(+M) = SO₃(+M) reaction. *Int. J. Chem. Kinet.*, 32, 317-339.
- Myrstad, T. and Fredriksen, G.R. (1998) Removal of Fe(CO)₅ from CO Gas as Detected by FTIR Spectroscopy. *Chem. Eng. Technol.*, 21, 297-299.

- Natarajan, J., Kochar, Y., Lieuwen, T., and Seitzman, J. (2009) Pressure and Preheat Dependence of Laminar Flame Speeds of H₂/CO/CO₂/O₂/He Mixtures. *Proc. Combust. Inst.* 32, in press, doi:10.1016/j.proci.2008.06.110
- Natarajan, J., Lieuwen, T., and Seitzman, J. (2007) Laminar Flame Speeds of H₂/CO Mixtures: Effect of CO₂ Dilution, Preheat Temperature, and Pressure. *Combust. Flame*, 151, 104-119.
- O'Connaire, M., Curran, H.J., Simmie, J.M., Pitz, W.J., and Westbrook, C.K. (2004) A Comprehensive Modeling Study of Hydrogen Oxidation. *Int. J. Chem. Kinet.*, 36, 603-622.
- Oppenheim, A.K. (1985) Dynamic Features of Combustion. *Phil. Trans. R. Soc. Lond. A*, 315, 471-508.
- Pang, G.A., Davidson, D.F., and Hanson, R.K (2009) Experimental Study and Modeling of Shock Tube Ignition Delay Times for Hydrogen–Oxygen–Argon Mixtures at Low Temperatures. *Proc. Combust. Inst.*, 32, in press, doi:10.1016/j.proci.2008.06.014
- Peeters, J. and Mahnen, G. (1973) Reaction Mechanisms and Rate Constants of Elementary Steps in Methane-Oxygen Flames. *Proc. Combust. Inst.*, 14, 133-146.
- Peschke, W.T. and Spadaccini, L.J. (1985) Determination of Autoignition and Flame Speed Characteristics of Coal Gases having Medium Heating Values. Electric Power Research Institute, Report EPRI AP-4291.
- Petersen, E.L. and Hanson, R. K. (2001) Nonideal Effects behind Reflected Shock Waves in a High-Pressure Shock Tube. *Shock Waves*, 10, 405-420.
- Petersen, E.L., Kalitan, D.M., Barrett, A.B., Reehal, S.C., Mertens, J.D., Beerer, D.J., Hack, R.L., and McDonell, V.G. (2007a) New Syngas/Air Ignition Data at Lower Temperature and Elevated Pressure and Comparison to Current Kinetics Models. *Combust. Flame*, 149, 244-247.

- Petersen, E.L., Lamnaouer, M., de Vries, J., Curran, H.J., Simmie, J., Fikri, M., Schulz, C., and Bourque, G. (2007b) Discrepancies between Shock-Tube and Rapid Compression Machine Ignition at Low Temperatures and High Pressures. *Proc. 26th International Symposium on Shock Waves*, Göttingen, Germany, July 2007, Paper No. P911.
- Rao, K.M., Spoto, G., Guglielminotti, E. and Zecchina, A. (1989) IR Investigation of $\text{Fe}(\text{CO})_5$ Adducts at the Surface of Silicalite, ZSM-5, Zeolite Y, and $\gamma\text{-Al}_2\text{O}_3$. *Inorg. Chem.*, 28, 243-247.
- Rasmussen C.L., Hansen, J., Marshall, P., and Glarborg, P. (2008) Experimental Measurements and Kinetic Modeling of $\text{CO}/\text{H}_2/\text{O}_2/\text{NO}$, Conversion at High Pressure. *Int. J. Chem. Kinet.*, 40, 454-480.
- Reehal, S.C., Kalitan, D.M., Hair, T., Barrett, A.B., and Petersen, E.L. (2007) Ignition Delay Time Measurements of Synthesis Gas Mixtures at Engine Pressures. *Proc. 5th US Combustion Meeting*, San Diego, CA, Paper No. C24.
- Reinelt, D. and Linteris, G.T. (1996) Experimental Study of the Inhibition of Premixed and Diffusion Flames by Iron Pentacarbonyl. *Proc. Combust. Inst.*, 26, 1421-1428.
- Rezaiyan, J. and Cheremisinoff, N.P. (2005) *Gasification Technologies: A Primer for Engineers and Scientists*. CRC Press, Boca Raton.
- Rozenstein, V.B., Gershenzon, Yu.M., Il'in, S.D., and Kishkovjitch, O.P. (1984) Reactions of HO_2 with NO, OH and HO_2 Studied by EPR/LMR Spectroscopy. *Chem. Phys. Lett.*, 112, 473-478.
- Rumminger, M.D. and Linteris, G.T. (2000) Inhibition of Premixed Carbon Monoxide-Hydrogen-Oxygen-Nitrogen Flames by Iron Pentacarbonyl. *Combust. Flame*, 120, 451-464.

- Rumminger, M.D. and Linteris, G.T. (2002) The Role of Particles in the Inhibition of Counterflow Diffusion Flames by Iron Pentacarbonyl. *Combust. Flame*, 128, 145-164.
- Rumminger, M.D., Reinelt, D., Babushok, V., and Linteris, G.T. (1999) Numerical Study of the Inhibition of Premixed and Diffusion Flames by Iron Pentacarbonyl. *Combust. Flame*, 116, 207-219.
- Sellevåg, S.R., Georgievskii, Y., and Miller, J.A. (2008) The Temperature and Pressure Dependence of the Reactions $\text{H} + \text{O}_2 (+\text{M}) \rightarrow \text{HO}_2 (+\text{M})$ and $\text{H} + \text{OH} (+\text{M}) \rightarrow \text{H}_2\text{O} (+\text{M})$. *J. Phys. Chem. A*, 112, 5085-5095.
- Shen, H.-P. S., Vanderover, J., and Oehlschlaeger, M.A. (2009) A Shock Tube Study of the Auto-Ignition of Toluene/Air Mixtures at High Pressures. *Proc. Combust. Inst.*, 32, in press, doi:10.1016/j.proci.2008.05.004
- Sivaramakrishnan, R., Comandini, A., Tranter, R.S., Brezinsky, K., Davis, S.G., and Wang, H. (2007) Combustion of CO/H₂ Mixtures at Elevated Pressures. *Proc. Combust. Inst.*, 31, 429-437.
- Slack, M.W. (1977) Rate Coefficient for $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$ Evaluated from Shock Tube Measurements of Induction Times. *Combust. Flame*, 28, 241-249.
- Snyder, A.D., Robertson, J., Zanders, D.L., and Skinner, G.B. (1965) Shock Tube Studies of Fuel-Air Ignition Characteristics. Report AFAPL-TR-65-93, Air Force Aeropropulsion Lab, Wright-Patterson.
- Sridharan, U.C., Qiu, L.X., and Kaufman, F. (1984) Rate Constant of the $\text{OH} + \text{HO}_2$ Reaction from 252 to 420 K. *J. Phys. Chem.*, 88, 1281-1282.
- Srinivasan, N.K., Michael, J.V. (2006) The Thermal Decomposition of Water, *Int. J. Chem. Kinet.*, 38, 211-219.

- Srinivasan, N.K., Su, M.-C, Sutherland, J.W., Michael, J.V., and Ruscic, B. (2006) Reflected Shock Tube Studies of High-Temperature Rate Constants for $\text{OH} + \text{NO}_2 \rightarrow \text{HO}_2 + \text{NO}$ and $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$. *J. Phys. Chem. A*, 110, 6602-6607.
- Strehlow, R.A. and Cohen, A. (1962) Initiation of detonation. *Phys. Fluids*, 5, 97-101.
- Ströhle J. and Myhrvold T. (2007) An Evaluation of Detailed Reaction Mechanisms for Hydrogen Combustion under Gas Turbine Conditions. *Int. J. Hydrogen Energ.*, 32, 125-135.
- Sun, H.Y., Yang, S.I., Jomaas, G., and Law, C.K. (2007) High-Pressure Laminar Flame Speeds and Kinetic Modeling of Carbon Monoxide/Hydrogen Combustion. *Proc. Combust. Inst.*, 31, 439-446.
- Sung, C.-J. and Law, C.K. (2008) Fundamental Combustion Properties of H_2/CO Mixtures: Ignition and Flame Propagation at Elevated Pressures. *Combust. Sci. Tech.*, 180, 1097-1116.
- Tepe, R.K., Vassallo, D., Jacksier, T., and Barnes, R.M. (1999) Iron Pentacarbonyl Determination in Carbon Monoxide. *Spectrochim. Acta B*, 54, 1861-1868.
- Terao, K. (1977) Explosion Limits of Hydrogen-Oxygen Mixtures as a Stochastic Phenomenon. *Jap. J. Appl. Phys.*, 16, 29-38.
- Troe, J. (2000) Detailed Modeling of the Temperature and Pressure Dependence of the Reaction $\text{H} + \text{O}_2 (+\text{M}) \rightarrow \text{HO}_2 (+\text{M})$. *Proc. Combust. Inst.*, 28, 1463-1469.
- Troe J. and Ushakov, V.G. (2001) Theoretical Studies of the $\text{HO} + \text{O} \leftrightarrow \text{HO}_2 \leftrightarrow \text{H} + \text{O}_2$ Reaction. II. Classical Trajectory Calculations on an Ab Initio Potential for Temperatures Between 300 and 5000 K. *J. Chem. Phys.*, 115, 3621-3628.

- Tse, S.D., Zhu, D.L., and Law, C.K. (2000) Morphology and Burning Fluxes of Expanding Spherical Flames in H₂/O₂/Inert Mixtures up to 60 Atmospheres. *Proc. Combust. Inst.*, 28, 1793–1800.
- Vanpee, M. and Shirodkar, P.P. (1978) Study of Flame Inhibition by Metal Compounds. *Proc. Combust. Inst.*, 17, 787-795.
- Voevodsky, V.V. and Soloukhin, R.I. (1965) On the Mechanism and Explosion Limits of Hydrogen-Oxygen Chain Self-Ignition in Shock Waves. *Proc. Combust. Inst.*, 10, 279-283.
- von Elbe, G. and Lewis, B. (1942) Mechanism of the Thermal Reaction between Hydrogen and Oxygen. *J. Chem. Phys.*, 10, 366-393.
- Walton, S.M., He, X., Zigler, B.T., and Wooldridge, M.S. (2007a) An Experimental Investigation of the Ignition Properties of Hydrogen and Carbon Monoxide Mixtures for Syngas Turbine Applications. *Proc. Combust. Inst.*, 31, 3147-3154.
- Walton, S.M., He, X., Zigler, B.T., and Wooldridge, M.S. (2007b) An Experimental Investigation of Iso-octane Ignition Phenomena. *Combust. Flame*, 150, 246-262.
- Wang, B.L., Olivier, H., and Grönig, H. (2003) Ignition of Shock-Heated H₂-Air-Steam Mixtures. *Combust. Flame*, 133, 93-106.
- Wang, H., You, X., Joshi, A.V., Davis, S.G., Laskin, A., Egolfopoulos, F., and Law, C.K. (2007) USC Mech Version II: High-Temperature Combustion Reaction Model of H₂/CO/C₁-C₄ Compounds. http://ignis.usc.edu/USC_mech_II.htm, May 2007.
- Westbrook, C.K. and Dryer, F.L. (1984) Chemical Kinetics Modeling of Hydrocarbon Combustion. *Prog. Energ. Combust. Sci.*, 10, 1-57.

- Wilhelm, D.J., Simbeck, D.R., Karp, A.D., and Dickenson R.L. (2001) Syngas Production for Gas-to-Liquids Applications: Technologies, Issues and Outlook. *Fuel Process. Technol.*, 71, 139-148.
- Williams, T.C. and Shaddix, C.R. (2007) Contamination of Carbon Monoxide with Metal Carbonyls: Implications for Combustion Research. *Combust. Sci. Tech.*, 175, 1225-1230.
- Yetter, R.A., Dryer, F.L., and Rabitz, H. (1991a) A Comprehensive Reaction Mechanism for Carbon Monoxide/Hydrogen/Oxygen Kinetics. *Combust. Sci. Tech.*, 79, 97-128.
- Yetter, R.A., Dryer, F.L., and Rabitz, H. (1991b) Flow Reactor Studies of Carbon Monoxide/Hydrogen/Oxygen Kinetics. *Combust. Sci. Tech.*, 79, 129-140.
- You, X., Wang, H., Goos, E., Sung, C.J., and Klippenstein, S.J. (2007) Reaction Kinetics of $\text{CO} + \text{HO}_2 \rightarrow \text{Products}$: Ab Initio Transition State Theory Study with Master Equation Modeling. *J. Phys. Chem. A*, 111, 4031-4042.
- Zhao, Z., Li, J., Kazakov, A., and Dryer, F.L. (2005) Temperature-Dependent Feature Sensitivity Analysis for Combustion Modeling. *Int. J. Chem. Kinet.*, 37, 282-295.
- Zheng, X.L. and Law, C.K. (2004) Ignition of Premixed Hydrogen/Air by Heated Counterflow under Reduced and Elevated Pressures. *Combust. Flame*, 136, 168-179.

TABLES

Table 1. List of reactions discussed in the text.

<i>Label</i>	<i>Reaction</i>
(R1)	$\text{H} + \text{O}_2 = \text{O} + \text{OH}$
(R2)	$\text{H} + \text{O}_2 (+\text{M}) = \text{HO}_2 (+\text{M})$
(R3)	$\text{HO}_2 + \text{HO}_2 = \text{H}_2\text{O}_2 + \text{O}_2$
(R4)	$\text{H}_2\text{O}_2 (+\text{M}) = \text{OH} + \text{OH} (+\text{M})$
(R5)	$\text{HO}_2 + \text{H}_2 = \text{H}_2\text{O}_2 + \text{H}$
(R6)	$\text{HO}_2 + \text{H} = \text{H}_2 + \text{O}_2$
(R7)	$\text{HO}_2 + \text{H} = \text{OH} + \text{OH}$
(R8)	$\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$
(R9)	$\text{HCO} + \text{M} = \text{H} + \text{CO} + \text{M}$
(R10)	$\text{HCO} + \text{O}_2 = \text{HO}_2 + \text{CO}$
(R11)	$\text{CO} + \text{HO}_2 = \text{CO}_2 + \text{OH}$
(R12)	$\text{HO}_2 + \text{OH} = \text{H}_2\text{O} + \text{O}_2$
(R13)	$\text{H}_2 + \text{OH} = \text{H}_2\text{O} + \text{H}$
(R14)	$\text{OH} + \text{H}_2 = \text{H}_2\text{O} + \text{O}$
(R13)	$\text{H}_2 + \text{OH} = \text{H}_2\text{O} + \text{H}$
(R14)	$\text{O} + \text{H}_2 = \text{H} + \text{OH}$
(R15)	$\text{H} + \text{OH} + \text{M} = \text{H}_2\text{O} + \text{M}$

FIGURE CAPTIONS

Figure 1. Explosion limit characteristics for stoichiometric H_2/O_2 mixtures. Classical limits (Lewis and von Elbe, 1987) are shown by the solid line. Calculations (using reaction rates from the model of Li et al., 2004) for the pressure-temperature boundaries determining the second explosion limit (dashed line) and the extended second explosion limit (dash-dot line) are also shown (see text). The filled circles denote the conditions, in temperature-pressure space, for the plots shown in Fig. 2.

Figure 2. Constant-volume adiabatic calculations (using the model of Li et al., 2004) for a stoichiometric H_2/O_2 system at 20 atm: (a) normalized temperature-time traces for two temperature conditions (solid line – 1000 K, dashed line – 1300 K) below and above the extended second limit (see Fig. 1); (b) characteristic reaction times as a function of temperature; overall activation energies (E_a) at temperatures above and below the extended second limit are listed and have been estimated by fitting the computed data to an equation of the form $t_c = A \exp(E_a/RT)$, where t_c is the characteristic time, R the universal gas constant, T the temperature, and A is a pre-exponential factor.

Figure 3. Comparison of H_2/O_2 second explosion limit experimental data (symbols) with the criterion $[\text{M}] = 2k_1/k_2$ computed using rate values obtained from the kinetic models listed (lines) for $\text{M} = \text{N}_2$. Data are for stoichiometric mixtures, obtained in a flow reactor (Mueller et al. 1999a), static reactors (Baldwin et al., 1967; Egerton and Warren, 1951; von Elbe and Lewis, 1942), and a well stirred reactor (Baulch et al., 1988). Experiments used 2:1 (mol) $\text{H}_2:\text{O}_2$ mixtures except the studies of Baldwin et al. (28% H_2 , 14% O_2 , 58% N_2 , mol) and Mueller et al. (1% H_2 , 0.5% O_2 , 98.5% N_2 , mol). The data have been modified to take into account the third body efficiencies of H_2 and O_2 relative to N_2 , efficiencies were taken from

von Elbe and Lewis (1942). The bold dash-dot line denotes the explosion boundary for a system containing water (10 mol %), calculated using the model of Li et al. (2004, 2007).

Figure 4. Temperature dependence of the low-pressure limit reaction rate of $\text{H}+\text{O}_2(+\text{M})=\text{HO}_2(+\text{M})$ for $\text{M} = \text{N}_2$. The recent evaluation of Baulch et al. (2005) is also plotted with associated uncertainties.

Figure 5. Temperature and pressure dependence of (R2) from recent evaluations for $\text{M}=\text{N}_2$. Solid lines represent the values of Fernandes et al. (2008); dashed lines are the recommendation of Sellevåg et al. (2008).

Figure 6. Comparison between measured (Mittal et al., 2006) and predicted RCM ignition delay times for a $(\text{H}_2+\text{CO})/\text{O}_2/\text{N}_2/\text{Ar} - 12.5/6.25/18.125/63.125$ (molar) mixture. R_{CO} is the fraction of CO in (H_2+CO) . Compressed conditions are 50 bar and 1044 K. Lines show the difference in the quality of model predictions when the rate of You et al. (2007) for (R6) is used in the model of Li et al. (2007). Modeling performed in accordance with the methods described in Mittal et al. (2006).

Figure 7. Rate constants for $\text{HO}_2+\text{OH}=\text{H}_2\text{O}+\text{O}_2$; ∇ – Peeters and Mahnen (1973); $\blacktriangledown$ – DeMore (1979); $\triangleleft$ – Lii et al. (1980); $\ast$ – Cox et al. (1981); $\triangle$ – Kurylo et al (1981); $\bullet$ – Braun et al. (1982); $\diamond$ – DeMore (1982); $\oplus$ – Goodings and Hayhurst (1988); $\square$ – Keyser (1988); $\blacktriangle$ – Hippler and Troe (1992) (reevaluation of data from Hippler et al., 1990); $\star$ – Hippler et al. (1995); $\circ$ – Kappel et al. (2002); $\times$ – Srinivasan et al. (2006); dashed line – rate expression of Sivaramakrishnan et al. (2007); solid line – fit by Chaos and Dryer (2008) considering the rate minimum measured by Hippler et al. (1995); dash-dot line – fit by Chaos and Dryer (2008) considering the rate minimum measured by Kappel et al. (2002). The figure insert provides details of data and rate fits at high temperatures.

Figure 8. Ignition delay times of syngas/air (Peschke and Spadaccini, 1985; Petersen et al., 2007a; Walton et al., 2007a) and hydrogen/air mixtures (Blumenthal et al., 1995). Conditions: 38.6% H₂ + 51.1% CO + 10.3% CO₂ + Air, $\phi = 0.5$, $16.5 < P < 28.9$ atm (Petersen et al, 2007a; shock tube), $11.9 < P < 23$ atm (Peschke and Spadaccini, 1985); 50% H₂ + 50% CO + Air, $0.33 < \phi < 0.6$, $5.0 < P < 5.3$ atm (Petersen et al., 2007a; flow reactor); $(6.7 < \text{H}_2 < 13.6\%) + (4.5 < \text{CO} < 9.1\%) + (16.2 < \text{O}_2 < 18.6\%) + (44.1 < \text{N}_2 < 63.2\%)$, $0.3 < \phi < 0.7$, $12 < P < 23.5$ atm (Walton et al., 2007a); 15% H₂ in air, $35 < P < 47$ bar (Blumenthal et al., 1995). Filled and open circles correspond to strong and weak ignition events, respectively (Blumenthal et al., 1995). All experimental data have been normalized to 20 atm assuming proportionality to P^{-1} . Long-dash lines correspond to ignition delay calculations performed under constant U , V assumptions using the model of Li et al. (2007) at 20 atm. The effect of pre-ignition linear pressure rise is shown for different pressure rise rates. To improve clarity, modeled results are not shown for times greater than 10 s although it is noted that constant U , V predictions can reach values of approximately 1000 s for the lowest temperatures ($T \sim 630$ K).

Figure 9. Hydrogen shock tube ignition delays (symbols) from a number of experimental studies compared against chemical kinetic predictions (lines) using the model of Li et al. (2007). Modeling performed using the reported gas temperature and a constant U , V thermodynamic assumption.

Figure 10. Shadowgraphs of the ignition process of 15% H₂ + 85 % air mixtures in a shock tube. (a) Mild ignition: 7.7 atm, 977 K, 100 μs separation between frames; (b) Strong ignition: 3.4 atm, 1096 K, 40 μs separation between frames. Note that these conditions lie on either side

of the extended second limit (see Fig. 1). Images have been adopted from Blumenthal et al. (1996).

Figure 11. Pressure profile during syngas ignition obtained from Reehal et al. (2007). Panel (b) “zooms” into the profile shown in (a) to show pre-ignition pressure rise.

Figure 12. Syngas ignition delay data (symbols) and predictions using the model of Li et al. (2007). Data are those of Reehal et al. (2007) for the mixture shown in Fig. 11 at an average pressure of 11.8 atm. The dashed line corresponds to modeling assuming constant U , V ; the solid line is the result of calculations using the pressure gradient shown in Fig. 11b and employing CHEMKIN-VTIM (see text). The gray symbol corresponds to the case shown in Fig. 11.

Figure 13. Laminar burning velocities of syngas mixtures. (a) $H_2:CO$ (1:1) in air at 1 atm; (b) $H_2:CO$ (1:3) + $O_2:He$ (1:7) mixtures at high pressure. Symbols are experimental measurements. The solid line shows predictions from the model of Li et al. (2007); the dashed line are results assuming a $Fe(CO)_5$ content of 200 ppm in the CO source (using the kinetic subset of Rumminger et al., 1999).

Figure 14. Measured and calculated unstretched laminar mass burning rates for $H_2 + (O_2:He - 1:11.5)$ flames at 10, 15, and 20 atm. Symbols are experimental data (Tse et al., 2000); solid lines are predictions using the model of Sun et al. (2007); dashed lines are predictions using the model of Li et al. (2007).

Figure 15. Infrared spectra of the carbon monoxide gas used in the experiments of Burke et al. (2007). The main absorption bands of $Fe(CO)_5$ are identified.

Figure 16. Laminar burning velocities of hydrogen mixtures at constant flame temperature (~ 1600 K) for various pressures; (a) $H_2/O_2/He$ (1.7/1/11.5) mixture, $\phi = 0.85$; (b) $H_2/O_2/Ar$

(5/1/9.5) mixture, $\phi = 2.5$. Symbols are experimental measurements from Burke et al. (2009a) (open circles) and Tse et al. (2000) (open triangles), lines are model results; Li et al. (2004, 2007) – bold solid line; Davis et al. (2005) – bold dashed line; Sun et al. (2007) – solid line; Konnov (2008) – dashed line.

Figure 17. Sensitivity of mass burning rates to rate parameters as a function of pressure for (a) $\text{H}_2/\text{O}_2/\text{He}$ mixtures (Fig. 16a); (b) $\text{H}_2/\text{O}_2/\text{Ar}$ mixtures (Fig. 16b).

Figure 18. Pressure dependence of temperature window sensitivities of burning rates to $\text{HO}_2 + \text{OH} = \text{H}_2\text{O} + \text{O}_2$ (R12) for the lean $\text{H}_2/\text{O}_2/\text{He}$ mixture of Fig. 16a. The laminar burning rate exhibits strong sensitivity to the reaction in the location of the local rate minimum of this reaction (see Fig. 7).

Figure 19. Comparison of relevant aspects of the flame structure at various pressures for (a) $\text{H}_2/\text{O}_2/\text{He}$ mixtures and (b) $\text{H}_2/\text{O}_2/\text{Ar}$ mixtures at the conditions shown in Fig. 16. Black lines represent H radical mole fraction and gray lines show the flux of H radicals through $\text{H} + \text{O}_2 = \text{O} + \text{OH}$ (R1) (solid line) and $\text{H} + \text{O}_2(+\text{M}) = \text{HO}_2(+\text{M})$ (R2) (dashed line). The temperature of the extended second limit temperature is marked by the vertical lines.

FIGURES

Figure 1

(a)

(b)

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

(a)

(b)

Figure 10

Figure 11

Figure 12

Figure 13

Figure 14

Figure 15

Figure 16

(a)

(b)

Figure 17

Figure 18

Figure 19

Low and Intermediate Temperature Oxidation of Ethanol and Ethanol-PRF Blends: An Experimental and Modeling Study

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1. Introduction

Ethanol fuels, particularly ethanol-gasoline blends, are increasingly being used to meet oxygenate requirements of the Clean Air Act as well as demands for renewable/alternative fuels. Despite extensive development at high and intermediate temperatures [1-10], the chemical kinetics of pure ethanol oxidation at low combustion temperatures and across the negative temperature coefficient (NTC) region is not well known. There remains a need to characterize this chemistry in light of its relevance to pollutant formation and knock behavior. Pollutants formed from ethanol-enriched fuels at lower temperatures, particularly the lower aldehydes, may have significant negative public health consequences [11]. Furthermore, while applied studies have demonstrated octane number enhancement for gasoline-ethanol or gasoline surrogate-ethanol blends compared to neat gasoline [12-14], the fundamental chemical coupling between ethanol and other fuel components under knock-prone conditions is virtually unexplored.

This short communication presents new experimental turbulent flow reactor oxidation results for neat ethanol at 12.5 atm and between ~525-900K. It is reported, for the first time, and the results described herein clearly demonstrate the lack of NTC chemistry in ethanol under knock-prone, engine relevant conditions. Initial kinetic modeling results for oxidation of ethanol in the presence of primary reference fuel (PRF) mixtures (n-heptane and iso-octane) are also

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presented to further demonstrate the behavior of ethanol/gasoline surrogate mixtures at these conditions.

Active low temperature reaction channels in ethanol oxidation

At lower temperatures, ethanol ($\text{C}_2\text{H}_5\text{OH}$) is consumed primarily through H atom abstraction to form one of three isomeric $\text{C}_2\text{H}_5\text{O}$ radicals. Unimolecular, homogeneous decomposition of $\text{C}_2\text{H}_5\text{OH}$ only becomes important at temperatures greater than $\sim 900\text{K}$. The branching ratios for the abstraction reactions

where $\text{X} = (\text{H}, \text{O}, \text{OH}, \text{HO}_2, \text{CH}_3, \text{O}_2)$, are key in determining overall oxidation behavior of ethanol as the proportion of each $\text{C}_2\text{H}_5\text{O}$ species governs subsequent reaction progress [2]. Reported branching ratios for the reactions (1) vary considerably (*e.g.* [5, 10, 15, 16]), and Li et al. [10] emphasize that rate constant selection for these reactions greatly affects predicted yields of the reaction intermediates.

Abstraction of secondary H atom leads to the α -hydroxyethyl radical ($\text{CH}_3\dot{\text{C}}\text{HOH}$), which reacts with O_2 or unimolecularly decomposes to yield a radical and acetaldehyde (CH_3CHO). Abstraction from the OH moiety yields ethoxy radical ($\text{CH}_3\text{CH}_2\text{O}\cdot$), which either β -scissions to form CH_3 and formaldehyde (CH_2O) or CH_3CHO and H. Ethoxy can also react with O_2 to form HO_2 and acetaldehyde.

Alternatively, abstraction of primary H atom gives a β -hydroxyethyl radical ($\dot{\text{C}}\text{H}_2\text{CH}_2\text{OH}$), which unimolecularly decomposes to OH and relatively stable ethylene (C_2H_4). A recent theoretical and experimental study of O_2 addition to β -hydroxyethyl [17], shows this reaction produces CH_2O , vinyl alcohol, or stabilized β -hydroxyethylperoxy radical; however, the

rate of O₂ addition is much slower than unimolecular decomposition and little reactant flux passes through this channel.

The acetaldehyde-forming CH₃CHOH and CH₃CH₂O paths can lead to degenerate branching initiated by oxygen addition to acetyl radical

The negative activation energy typically associated with the oxygen addition (2) may impart NTC behavior in ethanol given sufficient carbon flux through this low temperature acetaldehyde oxidation channel. Experiments investigating neat CH₃CHO oxidation in static [18] and flow [19] reactors show low temperature, NTC, and hot ignition characteristics for acetaldehyde (Fig. 1). Several earlier static reactor experiments for pure ethanol oxidation [20-22] find CH₃CHO to be a prominent intermediate produced prior to hot ignition, and Brown and Tipper [20] observed up to three cool flames in stoichiometric mixtures, which they attribute to degenerate branching of acetaldehyde oxidation products.

2. Experimental

Experiments were conducted in the Princeton Variable Pressure Flow Reactor Facility (VPFR). The VPFR operation is described elsewhere [23], and is only briefly discussed here. Experimental conditions for this study are reported in Table 1.

The pressurized reactor is essentially composed of a heated (near-adiabatic), mixer/diffuser followed by a constant area duct. At the mixer/diffuser inlet, vaporized fuel is

injected radially outward into a premixed stream of N_2/O_2 flowing radially inward to form a rapid mixing region. The mixing region is followed by a conical diffuser, expanding the flow cross sectional area into a downstream cylindrical reactor section ($\text{Re}_D \geq \sim 6000$). The flow is continually sampled using a hot water cooled, wall convection quench sampling probe positioned along the reactor axis. The extracted stream is transferred through heated Teflon sampling lines to various permanent gas analyzers and an FTIR spectrometer to measure stable organic species and water. Measurement accuracies for O_2 and carbonaceous species reported here are within and generally better than 4% of reading and carbon closure is typically better than 4%. The axial temperature of the reacting flow is measured at the same location as the sampling probe inlet using a silica coated, R-type thermocouple ($\pm 3\text{K}$ accuracy). The mixer/diffuser section can be displaced axially relative to the sampling location to vary reaction residence time ($\pm 5\%$ accuracy), determined from integration of an axial velocity/reaction length correlation. All chemicals used in the experiments reported here were 99+% pure.

3. Results and Discussion

3.1 Neat Ethanol

The major and minor stable species reactivity profile for neat ethanol oxidation at $\phi = 0.43$ is presented in Fig. 2, along with modeling results (discussed below). These experimental results clearly show that pure ethanol exhibits no NTC behavior under the conditions tested. Similar results are found for the near-stoichiometric ($\phi = 0.91$) reactivity profile of Run 2.

Quantitative destruction of $\text{C}_2\text{H}_5\text{OH}$ to ethylene and water (and to no other species) apparent at the lowest initial reaction temperatures shown in Fig. 2 is due to heterogeneous reactions in the mixer/diffuser region of the VPFR, not to low temperature chemistry or

homogeneous decomposition. Any radical mechanism responsible for generating ethylene and water would also generate CH_3CHO , CH_2O , and CH_4 in similar (tens of ppm) quantities through the reaction sequence beginning with reactions (1), while the experimental and computed rate constants [8] for the homogeneous decomposition

are orders of magnitude too slow at these temperatures to predict the observed species. Moreover, the heterogeneous decomposition of ethanol is verified both through additional pyrolysis experiments in the VPFR with all other conditions similar to Runs 1 and 2, and through experiments measuring constant temperature species profiles as a function of residence time (i.e. reactor length). In particular, results of Run 3 show that C_2H_4 and H_2O generation ceases outside the silica-foam mixer/diffuser, where the flow transitions to the 10 cm diameter quartz reactor section (see Fig. 3).

For Runs 1 and 2, as temperatures approach the hot ignition condition ($\sim 775\text{K}$), the expected products of H-atom abstractions (1) begin to appear and O_2 is consumed. At higher temperatures, ethanol and intermediate acetaldehyde are completely consumed, and the system follows well established small hydrocarbon oxidation kinetics.

The experimental results are compared to the predictions of the hierarchically developed, comprehensively validated, high and intermediate temperature ethanol kinetics model of Li et al. [10], with the addition of O_2 abstraction reactions (1) with rates recommended by Baulch et al. [24] as well as methyl peroxide chemistry (which shows some activity at the conditions of this study) taken from Petersen et al. [25]. Modeling results are time shifted to match the $\text{C}_2\text{H}_5\text{OH}$ mole fraction at hot ignition. Time shifting is a standard practice for modeling of VPFR data discussed at length in supplemental information to [26]. Aside from the effects of the

aforementioned heterogeneous reaction, the mechanism reproduces well the major and minor species profiles (Fig. 2). Since this model includes rates for all reactions (1) and (6), the model predictions further suggest that early ethanol destruction is not due to the gas phase chemistry.

3.2 Ethanol/PRF Blends

Reactivity results for neat ethanol indicate that no significant H atom abstraction takes place below $\sim 725\text{K}$; thus, accumulation and subsequent reaction of CH_3CHO only occurs at temperatures above conditions favoring negative temperature coefficient behavior [19]. While pure ethanol resists oxidation at low temperatures, it may still react at these conditions in the presence of a radical pool generated by added components known to exhibit low temperature chemistry. In particular, these components may generate radicals which can stimulate the CH_3CHO -forming pathways of ethanol at conditions favoring reactions (2) - (5). Modeling results for ethanol/PRF mixtures are presented below to illustrate radical pool coupling at lower temperatures.

Model Validation

Figure 4 compares predicted shock tube ignition delays to the experimental data of Fikri et al. [27] for a ternary mixture consisting of 18/62/20 (liq. vol. %) n-heptane/iso-octane/ethanol (Fuel B in [27]) to demonstrate the predictive capability of our combined ethanol-PRF model [10, 28]. It should be noted that the PRF submodel contains low temperature acetaldehyde oxidation reactions (2) - (5). No adjustments of kinetic parameters in the original models were performed to achieve the present quality of comparison.

Predicted ignition delays are generally within better than a factor of two of both the experimental data and the predictions using the mechanism of Ogura et al. [29]. Moreover, the effect of polytropic pressure increase at longer (≥ 1 ms) ignition delay times [30] has not been explicitly modeled; this effect tends to accelerate predicted ignition delay times at the lowest temperatures where the modeling differs most from the experiments.

Modeled ignition delays for the E20 blend are also compared in Fig. 4 to those of a PRF-only mixture with equal road octane number $((RON+MON)/2)$ of 92.3, as reported in [27]). The ethanolic component of the E20 mixture tends to retard ignition below ~ 775 K and accelerate ignition up to ~ 900 K. Beyond ~ 900 K there is little qualitative difference in the two sets of predicted ignition delays.

In agreement with experimental data, predictions of the combined model show lack of low temperature reactivity for $\phi = 0.91$ oxidation of an E85 blend with n-heptane (PRF 0), henceforth called E85.0, under the conditions of Run 4. Experimental and modeled species and temperature profiles share the same characteristics as described for Runs 1 and 2. This mixture is used here to investigate the chemical coupling of components that have very different low temperature characteristics, as detailed below.

Induction Chemistry at Low Temperatures

Flux analysis using the ethanol-PRF model described above to simulate the homogeneous oxidation of E85.0 (1000 ppm n-heptane) at 628 K and 12.5 atm shows that the low temperature reaction of n-heptane generates radicals that subsequently react with ethanol to form C_2H_5O radicals. Chemistry is initiated by

followed by the kinetically preferred H-atom abstraction of ethanol by HO₂ to α -hydroxyethyl

quickly forming acetaldehyde and regenerating HO₂

The straight chain behavior of reactions (8) and (9) leads to CH₃CHO and H₂O₂ as products, concurrently precluding further radical attack on n-heptane at low temperatures. Acceleration of the ignition delay time compared to E100 is due to infrequent branching through alternative paths, and flux and sensitivity analyses show the degenerate branching reactions of CH₃CHO do not play a significant role at these conditions.

Coupling of ethanol/n-heptane induction chemistry through HO₂ is also predicted in modeling of other ethanol/n-heptane blends at the same temperature, pressure, and n-heptane and O₂ concentrations (thereby keeping the same rate of initiation). However, chain branching is more pronounced as the concentration of ethanol falls. Overall rates of the Fuel + HO₂ reactions are within a factor of 3 between 500-1000K, so that large ethanol fractions in n-heptane are required to suppresses low temperature reactivity.

4. Conclusions

Experimentally measured stable species and temperature profiles for neat ethanol oxidation ($\phi = 0.43$ and 0.91) at 12.5 atm and temperatures ranging from 523-903K show that *pure ethanol has no low temperature reactivity* under the conditions examined; however, heterogeneous decomposition of ethanol on silica foam in the mixer/diffuser region of the experimental apparatus is observed. No similar effects are noted in the 10 cm diameter silica reactor section downstream of the mixer/diffuser. Aside from the effects of the noted

heterogeneous reaction, the existing ethanol oxidation model of Li et al. [10] predicts species reactivity profiles well over this temperature range. A combined ethanol/PRF model based on [10] and the PRF model of [28] agrees well with existing shock tube and flow reactor data for ethanol/PRF blends. Predictions using this combined model show that *fuel components with low temperature reactivity (i.e. n-heptane) stimulate a near-straight chain HO₂ induction cycle in sufficiently enriched ethanolic blends*. Although this HO₂ cycle, reactions (8) and (9), produce CH₃CHO as an intermediate, the low temperature reactions of CH₃CHO are not significant channels of carbon flux under the conditions considered. Instead, *low temperature reactivity is imparted by infrequent branching of the more reactive component (n-heptane)*. Future experimental work and model development is planned to further illuminate radical pool coupling for ethanolic fuels.

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References

1. K. Natarajan, K. A. Bhaskaran, Proc. 13th Int. Symp. Shock Tubes and Waves, SUNY Press, Niagra Falls, 1981, 834-842.
2. T. S. Norton, F. L. Dryer, Twenty-Third Symposium (International) on Combustion (1990) 179-185.
3. M. P. Dunphy, J. M. Simmie, J. Chem. Soc., Farad. Trans. 87 (11) (1991) 1691-1696.
4. M. P. Dunphy, P. M. Patterson, J. M. Simmie, J. Chem. Soc., Farad. Trans. 87 (16) (1991) 2549-2559.
5. N. M. Marinov, Int. J. Chem. Kinet. 31 (3) (1999) 183-220.
6. J. Li, A. Kazakov, F. L. Dryer, Int. J. Chem. Kinet. 33 (12) (2001) 859-867.
7. M. U. Alzueta, J. M. Hernandez, Energ. Fuel 16 (1) (2002) 166-171.
8. J. Li, A. Kazakov, F. L. Dryer, J. Phys. Chem. A 108 (38) (2004) 7671-7680.
9. P. Saxena, F. A. Williams, Proc. Combust. Inst. 31 (1) (2007) 1149-1156.
10. J. Li, A. Kazakov, M. Chaos, F. L. Dryer, Proc. 5th US Combustion Meeting, The Combustion Institute, San Diego, CA, 2007, Paper C26.
11. M. Z. Jacobson, Environ. Sci. Technol. 41 (11) (2007) 4150-4157.
12. M. S. Radwan, Performance and Knock Limits of Ethanol-Gasoline Blends in Spark-Ignited Engines, SAE Paper 850213, Society of Automotive Engineers, 1985.
13. W.-D. Hsieh, R.-H. Chen, T.-L. Wu, T.-H. Lin, Atmos. Environ. 36 (3) (2002) 403-410.
14. H. S. Yücesu, T. Topgül, C. Çınar, M. Okur, Appl. Therm. Engr. 26 (17-18) (2006) 2272-2278.
15. S. Xu, M. C. Lin, Proc. Combust. Inst. 31 (1) (2007) 159-166.
16. W. P. Hess, F. P. Tully, Chem. Phys. Lett. 152 (2-3) (1988) 183-189.

17. J. Zador, et al., Proc. Combust. Inst. 32, in press (2009).
18. E. W. Kaiser, C. K. Westbrook, W. J. Pitz, Int. J. Chem. Kinet. 18 (6) (1986) 655-688.
19. D. Zarubiak, Study of Acetaldehyde Combustion Kinetics in a Variable Pressure Flow Reactor, Masters Thesis, Princeton University, 1997.
20. J. Brown, C. F. H. Tipper, Proc. Royal Soc. (A) 312 (1510) (1969) 399-415.
21. C. F. Cullis, E. J. Newitt, Proc. Royal Soc. (A) 237 (1211) (1956) 530-542.
22. C. F. Cullis, E. J. Newitt, Proc. Royal Soc. (A) 242 (1231) (1957) 516-533.
23. J. Li, Experimental and Numerical Studies of Ethanol Chemical Kinetics, Ph.D. Thesis, Princeton University, 2004.
24. D. L. Baulch, et al., J. Phys. Chem. Ref. Data 34 (3) (2005) 757-1397.
25. E. L. Petersen, et al., Proc. Combust. Inst. 31 (1) (2007) 447-454.
26. Z. Zhao, M. Chaos, A. Kazakov, F. L. Dryer, Int. J. Chem. Kinet. 40 (1) (2008) 1-18.
27. M. Fikri, et al., Combust. Flame 152 (1-2) (2008) 276-281.
28. M. Chaos, et al., Proc. 5th US Combustion Meeting, The Combustion Institute, San Diego, CA, 2007, Paper E26.
29. T. Ogura, et al., Energ. Fuel 21 (6) (2007) 3233-3239.
30. M. Chaos, F. L. Dryer, Int. J. Chem. Kinet. submitted (2008).

Tables

Table 1: Experimental conditions for ethanol and ethanol oxidation in VPFR

Run Number	Pressure (atm)	Temperature [Range] (K)	ppm carbon ^a	ϕ^a	Residence Time (sec)
1	12.5	523-883	5409	0.43	1.8
2	12.5	523-903	5675	0.91	1.8
3	12.5	703	5880	pyrolysis	varies
4	12.5	498-903	5483	0.91	1.8

^abased on mole fraction measurements averaged across reactivity profile

List of Captions

Figure 1: Reactivity profile for acetaldehyde, $\phi = 1$, 10 atm, 5000 ppm initial fuel concentration.

After [19].

Figure 2: Reactivity profile for neat ethanol, conditions of Run 1. Modeling time shift is +300 msec.

Figure 3: Species profiles for C₂H₄ and H₂O at conditions of Run 3. Concentrations of CH₄, CH₂O and CH₃CHO were below detection limits at all points measured.

Figure 4: Comparison of experimental ignition delay times [27] with modeling predictions of this study for an E20 blend with PRF 77.5 (RdON = 92.3). Predictions for a PRF 92.3 mixture are additionally shown. Solid symbols - experimental measurements; open symbols – modeled constant U,V ignition delays using experimentally measured temperatures and pressures; solid lines – combined model constant U,V ignition delays at nominal pressures of 10, 30, and 50 bar; dashed lines - combined model constant U,V ignition delays at nominal pressures of 10, 30, and 50 bar for PRF 92.3.

Figures

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