Available online at www.sciencedirect.com

ScienceDirect

Proceedings of the Combustion Institute 36 (2017) 77–111

Proceedings of the Combustion Institute

www.elsevier.com/locate/proci

From theoretical reaction dynamics to chemical modeling of combustion

Stephen J. Klippenstein

Chemical Sciences and Engineering Division, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439, USA

Received 3 December 2015; accepted 25 July 2016
Available online 15 October 2016

Abstract

The chemical modeling of combustion treats the chemical conversion of hundreds of species through thousands of reactions. Recent advances in theoretical methodologies and computational capabilities have transformed theoretical chemical kinetics from a largely empirical to a highly predictive science. As a result, theoretical chemistry is playing an increasingly significant role in the combustion modeling enterprise. The accurate prediction of the temperature and pressure dependence of gas phase reactions requires state-of-the-art implementations of a variety of theoretical methods: ab initio electronic structure theory, transition state theory, classical trajectory simulations, and the master equation. In this work, we illustrate the current state-of-the-art in predicting the kinetics of gas-phase reactions through sample calculations for some prototypical reactions central to combustion chemistry. These studies are used to highlight the success of theory, as well as its remaining challenges, through comparisons with experiments ranging from elementary reaction kinetics studies through to global observations such as flame speed measurements. The illustrations progress from the treatment of relatively simple abstraction and addition reactions, which proceed over a single transition state, through to the complexity of multiwell multichannel reactions that commonly occur in studies of the growth of polycyclic aromatic hydrocarbons. In addition to providing high quality rate prescriptions for combustion modelers, theory will be seen to indicate various shortcomings in the foundations of chemical modeling. Future progress in the fidelity of the chemical modeling of combustion will benefit from more widespread applications of theoretical chemical kinetics and from increasingly intimate couplings of theory, experiment, and modeling.

Keywords: Theoretical chemical kinetics; Ab initio electronic structure theory; Transition state theory; Master equation; Combustion chemistry

1. Introduction

Recent years have seen an explosion in the number of studies using kinetic models to explore the chemistry of combustion. A survey of the 2015 volume of Combustion and Flame finds studies implementing kinetics models for biofuels (*methanol, ethanol, n-butanol, isobutanol, 2-methylbutanol, n-pentanol, 2- and 3-pentanol, dimethyl ether, tetrahydrofuran, 2,5-dimethylfuran, tetrahydropyran, diethylcarbonate, and tripropyleneglycol mono-methyl*

E-mail address: sjk@anl.gov

http://dx.doi.org/10.1016/j.proci.2016.07.100
1540-7489

ether), gasoline, diesel, and jet fuel surrogates and blends (*primary reference fuel, toluene reference fuel, gasoline surrogate, gasoline and ethanol, Real Fuel 2, n-heptane/toluene/methyl-pentanoate, diesel surrogate, and JP-10*), large alkanes (*pentane, n-hexane, n-heptane, 7-dimethyloctane, n-dodecane, hexadecane, and exo-tricyclodecane*), aromatics (*benzene, toluene, and styrene*), naphthenes (*methylcyclohexane and ethylcyclohexane*), foundational fuels (*hydrogen, carbon monoxide, syngas, methane, natural gas, propane, n-butane, ethylene, acetylene, propene, and C3–C5 aldehydes*), pollutants (*ammonia, methylnitrate, NO_2 and N_2O in methane, NOx in alcohols, carbon sulfides, sour gas, HCl and Cl_2, and O_3*), energetic materials (*HMX*), and fire inhibitors (*$C_3H_2F_3Br$, C_2F_5H, CCl_4, and CF_3H*). These modeling studies explore a variety of chemical problems including the development of new mechanisms for novel fuels, an improved understanding of ignition, low-temperature/cool-flame chemistry, the chemistry of surrogates and other fuel mixtures, the effect of additives and dopants on the chemistry, improvement of mechanisms for core fuels, the dependence of pollutant formation (soot, NOx, SOx, etc.) on fuel and on combustion conditions, the coupling of chemistry and fluid dynamics, and the role of ions in combustion.

This increased focus on chemical modeling arises from a variety of societal drivers, coupled with the ever-improving fidelity and thus utility of modeling efforts, and the continuing expansion in computational capabilities. Computational simulations of internal combustion engines require the coupling of chemical models for the conversion of the fuel into combustion products with numerical treatments of the fluid dynamics of reacting flows. Many recent efforts to meet the demands of improved fuel economy and reduced emissions focus on low temperature combustion schemes [1,2] where the chemical aspects of the simulations are particularly important. Similarly, the push to consider alternative fuels as a means for reducing net CO_2 emissions and improving our energy security requires detailed understanding of the connection between engine performance and fuel structure, with fuel chemistry being an integral part of this connection [3]. Chemical models for combustion are also of continuing importance for stationary combustors with oxy fuel [4] and MILD [5] combustion schemes continuing to be developed, and ever higher pressures being considered [6,7], again in response to efficiency and pollutant formation concerns.

Historically, engine simulations have by necessity employed very limited representations of either the chemistry or the fluid dynamics. Continuing advances in computational algorithms and hardware allow for simulations that employ more physically realistic treatments of both aspects of the problem [8,9]. As a result, such simulations are beginning to be used as engine design tools [10,11]. Continued improvements in the predictive accuracy of such simulations should greatly enhance their utility in efforts to reduce the number of expensive and time-consuming prototypes that need to be built.

Chemical models for combustion are used to describe not only the conversion of the fuel into oxidation products, but also the formation of various pollutants such as NOx, soot, and unburned hydrocarbons. Thus, comprehensive chemical models nowadays consist of thermochemical and transport properties for hundreds to thousands of species, together with rate coefficients for the thousands to tens of thousands of reactions that connect these species within the combustion environment. For example, as illustrated in Fig. S1, a survey of the 2015 volume of Combustion and Flame finds mechanisms with the number of species ranging from 10 to 3000 and the number of reactions ranging from 20 to more than 20,000. The largest mechanisms tend to focus on the low temperature chemistry of surrogate fuels, while the smaller mechanisms tend to be either reduced versions of these large mechanisms for utility in complex fluid dynamics simulations, or mechanisms that focus on the chemistry of small foundational fuels such as hydrogen, methane, syngas, and natural gas.

The fidelity of the full simulations naturally depends on the accuracy of the parameters that make up the chemical model. Theoretical chemical reaction dynamics has long been a key player in the development of quantitative models for the underlying elementary reaction rate coefficients [12–14]. Historically, theory has focused on interpreting and extrapolating data from experimentally accessible conditions to those of relevance to combustion. However, recent years have seen a dramatic improvement in the accuracy of a priori theoretical predictions due to improved algorithms and increased computational power. Indeed, the accuracy of high-level theoretical studies now often rivals that of experiment. As a result, theoretical predictions are now routinely incorporated in combustion mechanisms. Recently, theoretical analyses have even been integrated into the mechanism generation and development effort [15–23]. In this review, we illustrate the extent of this transformation of theoretical chemical kinetics from an empirical to a predictive science through sample applications to a range of elementary reactions of importance to combustion chemistry.

The overarching goal of the combustion chemical modeling enterprise is to provide a model that faithfully reproduces the chemical transformations that occur during the conversion of the fuel into products and pollutants for all relevant conditions of temperature, pressure, stoichiometry, and dilution. This goal is generally expressed via the production of a comprehensive model that accurately reproduces all available experimental observations