A hierarchical method for Bayesian inference of rate parameters from shock tube data: Application to the study of the reaction of hydroxyl with 2-methylfuran

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ABSTRACT

We developed a novel two-step hierarchical method for the Bayesian inference of the rate parameters of a target reaction from time-resolved concentration measurements in shock tubes. The method was applied to the calibration of the parameters of the reaction of hydroxyl with 2-methylfuran, which is studied experimentally via absorption measurements of the OH radical's concentration following shock-heating. In the first step of the approach, each shock tube experiment is treated independently to infer the posterior distribution of the rate constant and error hyper-parameter that best explains the OH signal. In the second step, these posterior distributions are sampled to calibrate the parameters appearing in the Arrhenius reaction model for the rate constant. Furthermore, the second step is modified and repeated in order to explore alternative rate constant models and to assess the effect of uncertainties in the reflected shock's temperature. Comparisons of the estimates obtained via the proposed methodology against the common least squares approach are presented. The relative merits of the novel Bayesian framework are highlighted, especially with respect to the opportunity to utilize the posterior distributions of the parameters in future uncertainty quantification studies.

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1. Introduction

The parameters appearing in rate constants for chemical reactions are commonly estimated through least squares or optimization approaches based on shock-tube, flame-speed or stirred-reactor data obtained experimentally (e.g., [1–5]). These methodologies aim at calibrating the rate parameters so as to minimize the misfit between the predictions and rates deduced from experimental measurements. The latter are also inferred quantities, generally estimated by minimizing the difference between the measured and simulated transient concentrations of selected species. In such a framework, the calibration of the chemical rate

expressions is based on data that are themselves the result of an optimization. This makes it difficult to quantify the impact of experimental errors or uncertainties in experimental conditions.

In the present work, we explore the application of a Bayesian inference formalism to calibrate the chemical rate expression for the reaction of 2-methylfuran with hydroxyl, based on the transient concentration of OH measured during a recent campaign of shock tube experiments [6]. The effort is motivated by a desire to take advantage of the capabilities afforded by Bayesian methods, specifically in accommodating noisy observations and enabling sequential learning and updating of prior information.

Due to these and other capabilities, Bayesian methods have received growing interest in kinetic calibration studies, e.g., [7–16].

In many cases, the application of Bayesian inverse methods has capitalized on advances in techniques developed in the field of uncertainty quantification (UQ) [17,18]. For example, effective

approaches for building efficient surrogate model representations [19–27] reduce the computational costs of inference significantly. These surrogate models have been exploited for accelerating the solution of optimal experimental design [28,29] and inverse problems [30,31] that are at the foundation of Bayesian methods.

In the present context, an additional motivation for the application of Bayesian methods concerns the details of shock tube experiments [6], which rely on thermal decomposition of tert-butyl-hydroperoxide (TBHP) in order to generate hydroxyl radicals behind the shock [32]. Specifically, the amount of TBHP that undergoes thermal decomposition in the shock tube is not known precisely and this uncertainty compounds other difficulties related to noisy signals and uncertain operating conditions, e.g., the temperature of the mixture behind the reflected shock. The presence of multiple sources of uncertainty is difficult to manage in a least squares (LS) or deterministic optimization context. The application of a Bayesian formalism may be beneficial in this regard, also.

In this work, we addressed the Bayesian calibration problem by first building a surrogate model representation of the experimental observable, the OH concentration, as function of uncertain inputs. Then, the uncertain rate parameters and the experimental conditions are calibrated in a *single-step* inference exercise.

Whereas this first approach proved suitable for the purpose of inferring the chemical rate parameters, success was limited due to difficulties in the treatment of noisy signals, handling of uncertainties in experimental conditions, and characterization of uncertainties in reaction rates. To overcome these difficulties, a hierarchical inference approach, featuring two steps, was developed. The hierarchical approach consists in applying the Bayesian inference methodology to infer the reaction rate in each shock tube experiment first, and then use the resulting posterior distributions as input to a second Bayesian inverse problem aimed at calibrating the parameters in the chemical rate expression.

The goal of the present paper is to outline the construction of the hierarchical inference approach, analyze its performance based on an application to the measured concentrations signals from recent experiments [6], and highlight its merits relative to the single-step approach.

The paper is organized as follows. In Section 2, the details of the reaction of hydroxyl with 2-methylfuran are addressed first. An in-depth discussion of the methodology that is customarily adopted in the processing of shock tube data is then presented in Section 3. In Section 4, we discuss the preliminaries for the Bayesian inference framework. The single-step and the two-step hierarchical methods are described together with their application to the inference of the rate parameters of the reaction of hydroxyl with 2-methylfuran in Sections 5 and 6, respectively. Finally, conclusions are presented in Section 7.

2. Target reaction, shock tube experiments, and reactor model

Increasing energy demand, fluctuating fuel prices, and environmental concerns are driving the development of alternative energy sources. Fuels derived from lignocellulosic biomass, categorized as second-generation biomass, have attracted considerable attention in the last decade. Among various fuels that can be produced from lignocellulose, furan and its alkylated derivatives are very promising due to their favorable combustion properties and relatively high energy density [33].

Prediction of the ignition and emission characteristics of furans requires knowledge of their chemical kinetics, including rates of elementary reactions. Detailed chemical kinetic models have been developed for furan [34] and its alkylated derivatives, 2-methylfuran (2-MF) [35] and 2,5-dimethylfuran (2,5-DMF) [36].

The reaction of hydroxyl radical with furan, 2-MF, and 2,5-DMF plays a key role in the high-temperature oxidation of these compounds. The rate coefficients of these reactions were experimentally measured by Elwardany et al. [6] in a recent shock tube study. Here, we consider the reaction of hydroxyl with 2-methylfuran only.

2.1. Target reaction

The reaction of OH radicals with 2-methylfuran (2-MF) is a key step in the overall oxidation of the compound. This reaction can either cause direct abstraction of H atoms from 2-MF or it can follow an addition-elimination pathway via the formation of an addition complex. At high temperatures (> 900 K), the direct abstraction route dominates and the addition route can be ignored. The direct abstraction of H atoms can take place either at the methyl branch (CH_3) or at the ring [35]:

$$2-MF + OH \xrightarrow{k_1} FurylCH_2 + H_2O \tag{R1}$$

$$2-MF + OH \xrightarrow{k_2} M_5F-2yl + H_2O \tag{R2}$$
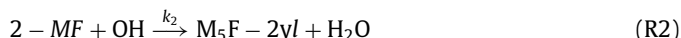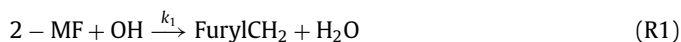
According to the rate constants proposed in [34,35], reaction R1 is the dominant pathway and accounts for 80% to 90% of the overall rate in the temperature range 800 to 1400 K. The branching ratio between the two pathways is obtained from *ab-initio* calculations [37].

In a recent study [6] by two of the authors of this paper, the rate constant for the overall reaction 2-MF + OH → products was measured in a shock tube facility over a range of temperatures (850–1330 K) and pressures (1–1.5 atm) for mixtures of 2-MF and tert-butyl-hydroperoxide diluted in argon. The measured rate constant was expressed in Arrhenius form as

$$k = 8.85 \times 10^{13} \exp(-2285/T) \quad cm^3 mol^{-1} s^{-1}. \tag{1}$$

Based on an error analysis, the overall uncertainty in the rate coefficient k in Eq. (1) was estimated to lie between +17% and −21% at 1150 K [6]. Primary sources of uncertainty included the rate coefficients of secondary reactions, fitting of measured OH profiles, mixture composition, and temperature behind the reflected shock.

2.2. Shock tube experiments

In Elwardany et al. [6], OH radicals were generated via the thermal decomposition of tert-butyl-hydroperoxide ($C_4H_{10}O_2$) according to the reaction

$$C_4H_{10}O_2 \longrightarrow C_4H_9O + OH. \tag{R3}$$

At the high temperatures considered in the study, the decomposition of tert-butyl-hydroperoxide (TBHP) is much more rapid than the consumption of OH. The amount of hydroxyl radicals available to react with 2-MF depends on the initial amount of TBHP and the rate of its thermal decomposition.

High-sensitivity, time-resolved measurements of the concentration of OH radicals were performed via absorption spectroscopy in the ultraviolet region near 306 nm. Following shock-heating, experimental data were collected using a high-resolution (14 bit) data acquisition system at a sampling rate of 2.5 MHz.

In this work, the raw data from 14 shock tube experiments at various temperatures and pressures are used (see supplementary material). Experiments were performed under *pseudo first-order* conditions by ensuring that the concentration of 2-MF exceeded by at least ten times that of OH. In addition, the composition of the test mixture was chosen in order to maximize the sensitivity of the concentration of OH to the target abstraction reaction. A complete list of the conditions for the experiments is provided in Table 1 alongside the overall rate constant k recommended in [6].

For the set of shock tube experiments 1 through 4, the test mixture (mixture A) consisted of 258 ppm 2-MF, 12 ppm TBHP, 32