

# The Importance of Relative Reaction Rates in the Optimization of Detailed Kinetic Models

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**ABSTRACT:** Numerous mathematical tools intended to adjust rate constants employed in complex detailed kinetic models to make them consistent with multiple sets of experimental data have been reported in the literature. Application of such model optimization methods typically begins with the assignment of uncertainties in the absolute rate constants in a starting model, followed by variation of the rate constants within these uncertainty bounds to tune rate parameters to match model outputs to experimental observations. The present work examines the impact of including information on relative reaction rates in the optimization strategy, which is not typically done in current implementations. It is shown that where such rate constant data are available, the available parameter space changes dramatically due to the correlations inherent in such measurements. Relative rate constants are typically measured with greater relative accuracy than corresponding absolute rate constant measurements. This greater accuracy further reduces the available parameter space, which significantly affects the uncertainty in the model outcomes as a result of kinetic parameter uncertainties. We demonstrate this effect by considering a simple example case emulating an ignition event and show that use of relative rate measurements leads to a significantly smaller uncertainty in the output ignition delay time in comparison with results based on absolute measurements. This is true even though the same range of absolute rate constants is sampled in each case. Implications of the results with respect to the maintenance of physically realistic kinetics in optimized models are discussed, and suggestions are made for the path forward in the refinement of detailed kinetic models. Published 2016. This article is a U.S. Government work and is in the public domain in the USA. *Int J Chem Kinet* 48: 358–366, 2016

## INTRODUCTION

The development of detailed chemical kinetic models has seen tremendous growth in recent years, partic-

ularly in the field of combustion, where one of the interests is in predicting and quantifying the effect of a fuel's composition on its suitability for a particular engineering application [1,2]. The need for such predictive models is in part related to the new fuel blends that are emerging as the marketplace assimilates alternative fuels such as shale oil, synthetic Fischer–Tropsch fuels, and a variety of existing and proposed biofuels [3–7].

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Large-scale testing of all possible fuel compositions is a daunting and expensive task, and the development of reliable predictive kinetic models represents an attractive alternative.

An important issue is the development of methods to both quantify uncertainties in the model predictions and adjust the input parameters of significance to be consistent with the extant experimental and computational data. Of these input parameters, reaction rate constants are key determinants of the flow of mass and energy through the system and thus strongly influence the accuracy of a particular model. While the elementary reactions that comprise the kinetic models have unique and universally applicable rate constants under defined conditions, the actual values may not be well established, and there is always an associated uncertainty. The development of trustworthy simulations requires the correct treatment of the rate constants and their uncertainties within the procedures used to validate and improve the kinetic models.

Historically, combustion models were assembled hierarchically [8–12], beginning with small systems and subsequently expanding to larger fuel molecules. In early work, the rate constants found to most impact the model outcomes were typically evaluated and ascribed a “best” value by individual kineticists [8–11] or panels of experts [13–15] convened for that purpose. However, large numbers of reactions are required to realistically describe the chemistry of fuels, and experimental determinations of rate constants are dwindling. Over the past 20 years, it has become common to use automated or semiautomated mechanism generators with rate constants estimated using various combinations of rate rules and computational chemistry [12,16–22]. To compensate for the lack of evaluated measurements, researchers have sought to develop methods to determine parameter values on the basis of a wider set of experimental information, including global experimental observations such as ignition delay times, flame speeds, species profiles, and other observables that can be linked to the detailed chemistry. Such procedures, which adjust model parameters (such as rate constants and transport properties) within their uncertainty bounds to better fit multiple sets of data, are often termed model optimizations.

The problem of optimization is in part made difficult by the complexity of the kinetic models, which for large fuels can involve hundreds of species and several thousand reactions [23,24]. Various approaches to this problem have been suggested over the years. Many of the general ideas are traceable to the early work of Frenklach [25], which was further developed as solution mapping methods [26], and later used in optimizations of methane combustion chemistry [27–29]. Nu-

merous researchers have since suggested other mathematical techniques to optimize rate constants by comparison of available experimental data with model predictions [30–34]. Such methods commonly employ a starting chemical reaction set with a preassigned set of uncertainties in the model rate constants; parameter values are then adjusted on the basis of mathematical formalisms that compare experimental and model results. Current state-of-the-art model development and optimization techniques have been discussed by Turanyi and Tomlin [35] in their 2014 book and by Wang and Sheen [36] in their 2015 review.

In the above methods, the rate constants and their uncertainties are often described solely in terms of their absolute values without regard for correlations with other model inputs. As kineticists and evaluators of kinetic data, we have some concerns about this procedure, in particular the possible consequences of treating *relative* rate constant information as data from absolute measurements and the subsequent impact on the optimized model outputs and their respective uncertainties.

Recent work on uncertainty quantification in combustion models includes that of Nagy and Turanyi [37], and Nagy et al. [30], who considered uncertainties related to the temperature dependence of Arrhenius parameters. Prager et al. [38] examined the effects of correlations in rate rules, for which little or no experimental data are available and found improvement in modeled ignition delay times when correlations were considered; Cai and Pitsch [39] have considered similar effects in the optimization of models of *n*-pentane combustion. In this work, we examine the impact of incorporating knowledge of relative rates of reaction typical of experimental relative rate measurements into the model optimization strategy. The measurement of relative rate constants commonly yields lower relative uncertainties than the independently measured ( $k \pm \sigma$ ) of the base reaction, which can lead to a derived rate constant that is quite different than if they were two independent measurements. Using a simple example model, we look at how such correlations are likely to affect uncertainties in model predictions. We close with a brief discussion of the implications for the maintenance of physically realistic kinetic models when applying optimization procedures and a possible path forward in the refinement of kinetic models.

## APPROACH AND METHODOLOGY

Hundreds of chemical systems have been kinetically modeled, many of which have multiple proposed

**Table I** Reaction Set Used in the Kinetics Model

Reaction	Rate Constant <sup>a</sup>	Reference and Notes
$C_4 \rightarrow 2H + 2C=C$	261.7	0.01 × 2004OEL/DAV [40], adjusted
$C_4 \rightarrow 2CH_3 + C=C$	279.0	0.01 × 2004OEL/DAV [40], adjusted
$2CH_3 \rightarrow C_2$	$6 \times 10^{-11}$	Pressure dependent, estimated from available data [41] for modeled conditions
$CH_3 + H \rightarrow C$	$2 \times 10^{-10}$	1994BAU/COB [14] pressure dependent, estimated for modeled conditions
$H + OH \rightarrow H_2O$	$2 \times 10^{-10}$	2008SEL/GEO [42] pressure dependent, estimated for modeled conditions
$H + O_2 \rightarrow HO_2$	$3 \times 10^{-13}$	1992BAU/COB [13] pressure dependent, estimated for modeled conditions
$H + O_2 \rightarrow OH + O$	$1.13 \times 10^{-12}$	2005MIL/PIL [43]
$H + C_4 \rightarrow H_2 + H + 2C=C$	$1.30 \times 10^{-11}$	$3.0 \times 10^{-11}$ total rate; branching ratio = 0.77 [44]
$H + C_4 \rightarrow H_2 + CH_3 + C-C=C$	$1.70 \times 10^{-11}$	$3.0 \times 10^{-11}$ total rate; branching ratio = 1.3 [44]
$H + C_2 \rightarrow H_2 + H + C=C$	$0.6 \times k_{C_4H}$	$k$ for C2 and C4 assumed constant per H
$H + C \rightarrow H_2 + CH_3$	$0.4 \times k_{C_4H}$	$k$ for C and C4 assumed constant per H
$OH + C_4 \rightarrow H_2O + H + 2C=C$	$k_{OH-H}$	See Table II for $k$
$OH + C_4 \rightarrow H_2O + CH_3 + C-C=C$	$k_{OH-CH_3}$	See Table II for $k$
$OH + C_2 \rightarrow H_2O + H + C=C$	$0.6 \times k_{OH-H}$	See Table II for $k$
$OH + C \rightarrow H_2O + CH_3$	$0.4 \times k_{OH-H}$	See Table II for $k$
$O + C_4 \rightarrow OH + H + 2C=C$	$k_{O-H}$	See Table II for $k$
$O + C_4 \rightarrow OH + CH_3 + C-C=C$	$k_{O-CH_3}$	See Table II for $k$
$O + C_2 \rightarrow OH + H + C=C$	$0.6 \times k_{O-H}$	See Table II for $k$
$O + C \rightarrow OH + CH_3$	$0.4 \times k_{O-H}$	See Table II for $k$
$O + H_2 \rightarrow OH + H$	$3.13 \times 10^{-12}$	1992BAU/COB [13]
$OH + H_2 \rightarrow H_2O + H$	$6.79 \times 10^{-12}$	1992BAU/COB [13]
$H + H_2O \rightarrow H_2 + OH$	$1.39 \times 10^{-12}$	1992BAU/COB [13]
$O + H_2O \rightarrow 2OH$	$2.81 \times 10^{-12}$	1991LIF/MIC [45]

<sup>a</sup>All rate constants are in units of  $\text{cm}^3$ ,  $\text{molecules}^{-1}$ , and  $\text{s}^{-1}$  as appropriate.

models that differ in their reaction sets and the proposed rate constants. It is not feasible, nor do we think it necessary, to individually analyze each system to examine our thesis. Rather we begin with the proposal that the qualitative behavior can be made evident simply by working with a small representative model that incorporates “typical” features of a combustion system and results in a prediction of some “typical” global behavior of interest.

### Kinetics Model

A simple set of reactions emulating an ignition event in a typical combustion system was constructed as shown in Table I. As noted above, the reaction set is not intended to represent a fully realistic model but rather a minimally complicated system that is computationally convenient and facilitates comparisons between analyses using absolute and relative measurements. Except in a few cases noted in the table, rate constant values were taken directly from the literature without adjust-

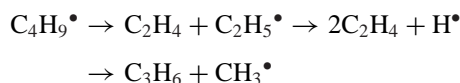
ment. The given reactions represent a simple chain reaction initiated by the loss of H-atoms from a model reactant “fuel,” which is simply designated  $C_4$ . Chain branching, e.g.,  $H + O_2 \rightarrow OH + O$ , ultimately leads to an “ignition” indicated by a rapid increase in the concentration of “reactive” H, O, and OH radicals. In competition with chain branching are terminations that occur if reactive radicals are converted to  $CH_3$ , a species which has much smaller H abstraction rate constants and is therefore assumed to be unreactive toward the fuel in this simplified system. The remaining steps represent the reactions of the reactive radicals with the fuel and the formation of radical–radical recombination products (shown as  $C_2$  and C). Reactions of stable closed-shell species such as  $H_2O$  formed from abstraction reactions in this system are not included. The reactive radicals are assumed to react with  $C_4$  to either form H or  $CH_3$  together with an alkene species that is not further modeled. Such a branching is meant to mimic the abstraction of H from an alkane by a reactive species  $X^*$  ( $X^* + C_4H_{10} \rightarrow XH + C_4H_9^*$ ) followed

**Table II** Rate Constants Varied in Models

$k^a$	Rate constant, $\text{cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$	Reference and Notes
$k_{\text{OH-CH}_3}$	$2.72 \times 10^{-11}$	1986COH/WES [46], $k_{\text{total}} = 5.0 \times 10^{-11}$
$k_{\text{OH-H}}$	$2.28 \times 10^{-11}$	1986COH/WES [46], $k_{\text{total}} = 5.0 \times 10^{-11}$
$k_{\text{O-CH}_3}$	$5.05 \times 10^{-11}$	Ibid., 1:1 branching, $k_{\text{total}} = 1.1 \times 10^{-10}$
$k_{\text{O-H}}$	$5.05 \times 10^{-11}$	Ibid., 1:1 branching, $k_{\text{total}} = 1.1 \times 10^{-10}$

<sup>a</sup>See Table I for the corresponding chemical equations.

by rapid decomposition of the resulting alkyl radicals:



These two decomposition reactions lead either to a radical (H) that leads to chain branching or, alternatively, to a species ( $\text{CH}_3$ ) that is assumed to be stable in this system. The differing pathways are determined by the site where the initial H abstraction occurs. Branching ratios for such abstraction processes represent one example of the type of relative rate information that is available in the literature. For example, in recent shock tube experiments branching values for the H + *n*-butane reaction have been measured with high precision on the basis of the final alkene product concentrations, which map cleanly to the location of the initial H abstraction under the conditions of the study [44]. Experimental relative rate data are similarly available for other attacking radicals and fuels, e.g., reaction of OH with ethanol [47], 2-propanol [48], and neopentyl alcohol [49].

In the kinetic model of Table I, the radical concentrations in the system as a function of time show a characteristic rapid increase followed by a rapid decrease. We have treated the rapid increase in the radical concentrations as an “ignition” with a corresponding ignition delay time that depends sensitively on the rate constants used in the model. In this way, the system represents a very simple combustor that is conducive to statistical sampling techniques with minimal additional interference from other reactions.

### Calculations and Statistical Sampling

Calculations were performed using Cantera 2.1.2 via the Python interface [50]. The system was modeled as a simple homogeneous constant volume ideal gas reactor at a constant temperature. Average reaction rate constants were calculated from published Arrhenius parameters at a temperature of 1500 K, and the system pressure was set to 10 bar. For simplicity, all rate constants were held constant without consideration of

pressure changes as the system evolves. Initial concentrations were set to  $4.65 \times 10^{18} \text{ cm}^{-3}$  and  $7.15 \times 10^{17} \text{ cm}^{-3}$  for  $\text{O}_2$  and  $\text{C}_4$ , respectively, for a stoichiometric (assuming  $\text{C}_4 = \text{C}_4\text{H}_{10}$  for the purpose of determining the equivalence ratio) fuel–air mixture.

For each model run, concentration profiles of the radical species at 1600 time points over 4 ms were calculated, and the ignition delay time was determined by finding the time at which the one-point discrete difference in the OH concentration was at a maximum. The other reactive radicals, H, and O, gave identical ignition delay times.

The uncertainty in the ignition delay time from this model was determined by repeatedly running the simulation while randomly varying the rate constants in Table II within their assumed uncertainties, and determining the standard deviation of the resulting ignition times. Two sets of calculations were performed. For the reactions that form H-atom ( $k_{\text{O-H}}$  and  $k_{\text{OH-H}}$ , where the notation separates with a dash the attacking radical and the resulting radical of interest), the value of  $k$  used in the model was determined by multiplying the average value in the table by a sample from a log normal distribution with a zero mean and standard deviation of 0.50, corresponding to an assumed 50% 1- $\sigma$  uncertainty. The  $\text{CH}_3$ -forming reaction rate constants ( $k_{\text{O-CH}_3}$  and  $k_{\text{OH-CH}_3}$ ) were calculated either by a similar independent sampling (the “absolute” case) or using the branching ratio with sampling that represents the lower uncertainty in the relative rate constants (the “relative” case).

For the “relative” case, the rate constants for the reactions that form  $\text{CH}_3$  ( $k_{\text{O-CH}_3}$  and  $k_{\text{OH-CH}_3}$ ) were determined by multiplying the sampled H atom rate constant by the average branching ratio (i.e.,  $k_{\text{x-H}}/k_{\text{x-CH}_3}$ ) and a sample from a log normal distribution with zero mean and standard deviation of 0.05, corresponding to a 10%  $2\sigma$  uncertainty in the branching ratio. In the “absolute” calculations, the values of  $k_{\text{O-CH}_3}$  and  $k_{\text{OH-CH}_3}$  were calculated from the average rate constant and a zero-mean log normal distribution with standard deviation of 0.5025, corresponding to the combined relative uncertainties of the H-atom rate constants and the assumed branching ratio uncertainty.

For both sets of calculations, 10,000 individual runs were performed, and the individual standard deviations in the resulting ignition delay times were calculated.

## RESULTS AND DISCUSSION

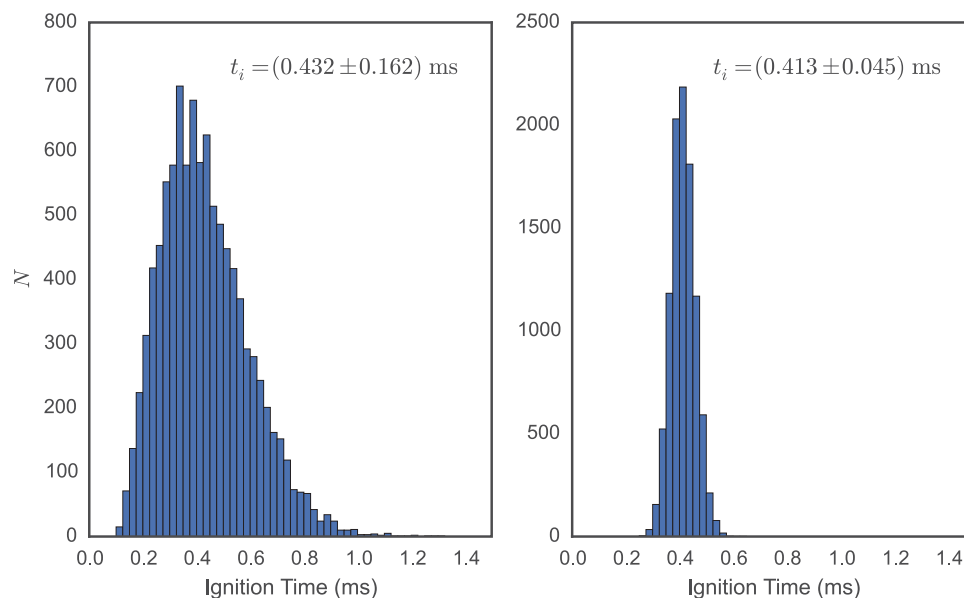
Shown in Fig. 1 are the results for ignition delay times under the absolute and relative rate constant sampling conditions. Figure 1 demonstrates for the simple system shown in Table I that the incorporation of relative rate information into the model leads to a small shift in the modeled ignition delay time compared with the absolute case. Most striking, however, is the reduction of the standard uncertainty in the model prediction by almost a factor of four. This is true despite the fact (Fig. 2) that the histograms of the individual rate constants are essentially identical in both mean and standard deviation for both cases.

Plotting the joint histograms,  $k_{\text{OH-H}}$  versus  $k_{\text{OH-CH}_3}$  and  $k_{\text{O-H}}$  versus  $k_{\text{O-CH}_3}$  (Fig. 3) reveals, in the relative case, the highly correlated parameter spaces for the varied rate constants. The solid lines in the figure indicate the encompassed areas at the respective 95% confidence intervals and display the vastly reduced space that is consistent with the assumed knowledge of the rate constants in the relative analysis. This highlights that the use of any model optimization procedure that ignores relative rate information will lead to a much less constrained result. Equally problematic, optimization procedures that treat the rate constants that were measured as relative rates as if they were independently

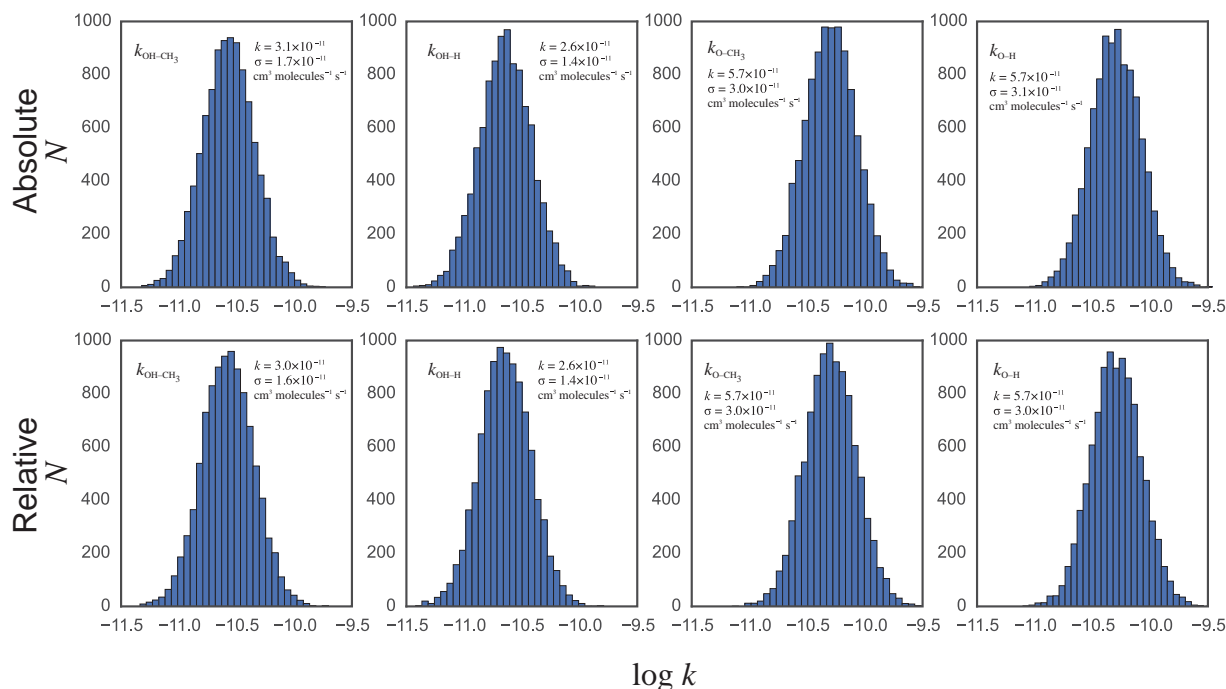
determined are allowing rate constant pairs that are not physically realistic. In complex systems, particularly when values are optimized on global experiments that are less directly connected to the detailed chemistry, one would anticipate that many of the resulting rate constant pairs will fall outside of the parameter space allowed by the relative rate information. This has significant implications for the fidelity of the derived models.

The above results are illustrative only. The exact degree to which the inclusion of relative rate information will change the uncertainty of a particular model prediction will naturally vary with the chemical system, the sensitivity of the result to the involved rate constants, and the available information on the relative and absolute rates. Nonetheless, it is critical to include all of this information in constraining any optimization to ensure that the input and output rate constants are fully consistent with the available experimental observations.

The present analysis assumes that relative rates and branching ratios can be experimentally measured with much higher accuracy than one can determine the absolute rate constants. While measurements must be assessed on a case-by-case basis, this is the usual situation for experiments that establish direct competitions and follow distinct products with an accurate analytical technique: In work from this laboratory, for example, uncertainties of around 10% ( $2\sigma$ ) in relative values are common [44,51–56], and such results are not dissimilar to measurements reported elsewhere in the literature [41,57]. In contrast, it is difficult to measure absolute



**Figure 1** Histograms of ignition delay times calculated using absolute (left) and relative (right) rate constants.



**Figure 2** Histograms of sampled rate constants in simulations for absolute (top row) and relative cases (bottom row).

rate constants with accuracies close to this level, particularly at the high temperatures most pertinent to combustion processes. Even if one assumes equal uncertainties in the relative and absolute measurements, the correlation between values ensures that the joint parameter space is reduced for relative measurements.

As noted in the Introduction, current optimization methods generally treat reaction rates as independent of each other and draw conclusions based on this assumption. For instance, in their recent review of uncertainty quantification in combustion models, Wang and Sheen [36] ask to what extent one can rely on first-principles approaches to combustion modeling and suggest that current levels of measurement accuracy may be insufficient to achieve truly predictive models. While the question remains valid, their arguments are based on the assumption of independent rate constant measurements, whereas the present analysis suggests that significantly better predictions might be expected if information on relative rates is incorporated.

### Modifications of Parameter Space Based on Available Data

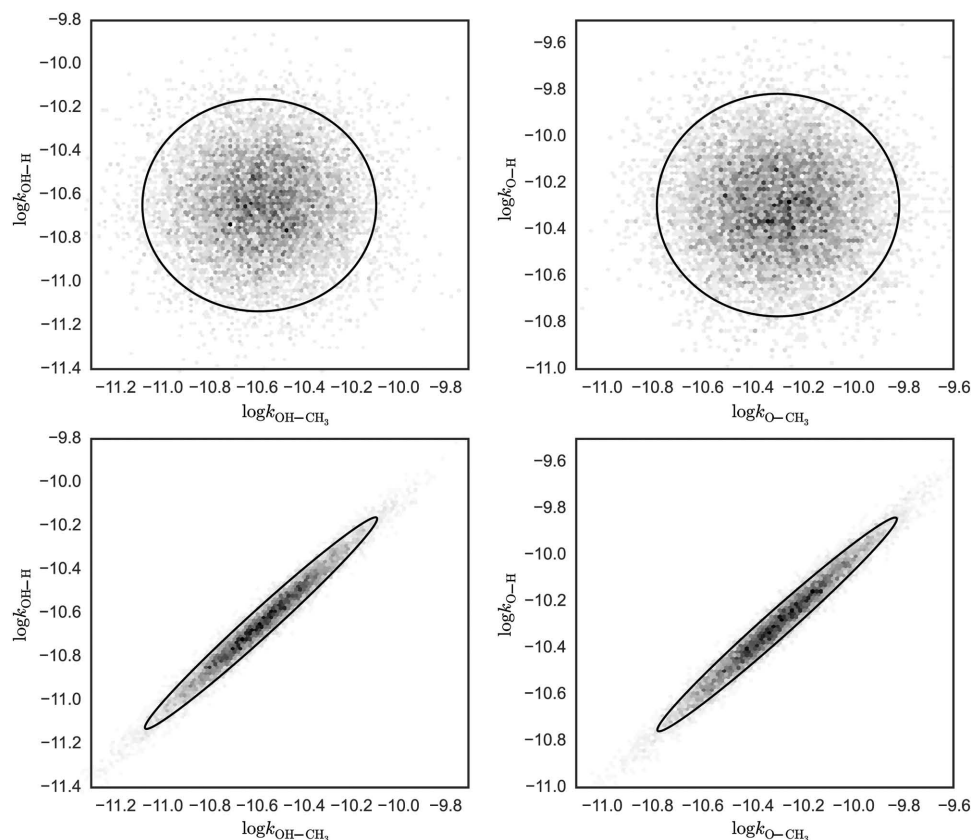
In this work, we have simulated two different cases to accentuate the need to consider data that are measured purely independently (absolute rate constants) separately from data derived from relative rate measurements (relative rate constants). These two cases,

now called absolute/absolute and absolute/relative in this discussion to emphasize how each rate constant was measured or determined, sample dramatically different parameter spaces, as shown in the upper and lower panels of Fig. 3, respectively. However, in actual practice, the available rate information may not always correspond to these situations, and some further consideration is warranted.

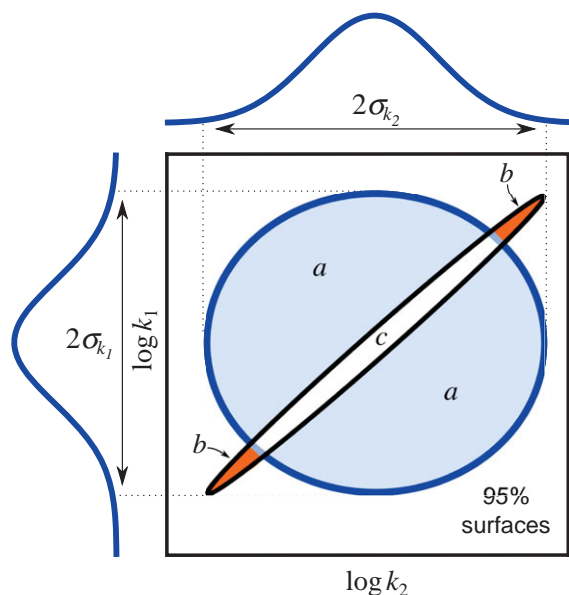
To facilitate discussion, in Fig. 4 we have schematically shown 95% surfaces of the simulated joint probability distributions for each of the cases described above, where  $k_1$  is always measured as an absolute rate constant and  $k_2$  is either an independent absolute measurement or is derived relative to  $k_1$ . The isopleths shown can be compared to the solid lines in Fig. 3. In Fig. 4, the absolute/absolute case corresponds to the broad ovoid encompassing regions *a* and *c*, and the absolute/relative case is parameterized by the narrower ovoid consisting of the *b* and *c* regions. In this diagram, we have assumed that the projected uncertainty of  $k_2$  is the same whether or not it is treated as an absolute or relative value, just as we have done in the kinetic simulations, although there is no general reason this should be true.

In both cases, the projection of the joint probability distribution on either axis leads to the identical, fully Gaussian uncertainty distributions for each rate constant. Notice that in the absolute/relative case, the large correlation between  $k_1$  and  $k_2$  leads to a narrower joint





**Figure 3** Two-dimensional histograms showing for the absolute (top) and relative (bottom) cases the joint parameter spaces  $k_{\text{OH-H}}$  versus  $k_{\text{OH-CH}_3}$  and  $k_{\text{O-H}}$  versus  $k_{\text{O-CH}_3}$ .



**Figure 4** Schematic view of parameter space for absolute/absolute ( $a + c$ ), absolute/relative ( $b + c$ ), and absolute/absolute + relative ( $c$ ).

probability distribution, part of which extends outside the range of the absolute/absolute case. This is because  $k_2$  is measured only relative to  $k_1$ , and therefore the culling of the tails of the joint distribution along the  $k_1 = k_2$  axis (region  $b$  in Fig. 4), that would be accomplished by an absolute measurement of  $k_2$  does not occur. However, it is not unusual to have a set of three measurements consisting of an absolute measurement of  $k_1$ , an absolute measurement of  $k_2$ , and a measurement of  $k_1/k_2$  [i.e., the absolute/(absolute+relative) case], which then leads to a smaller region of parameter space (region  $c$  in the figure) that remains consistent with the kinetics data. Careful consideration of all of the available data, including both the individual data point's uncertainties and measurement type, is critical in accurately defining rate constants that are consistent with available experimental data. Specific recommendations for implementing these restrictions is outside the scope of this paper, and a future publication will explore the implications of these restrictions using experimental data and a broader, more expressive, chemical kinetics model.

## Conclusions and Final Remarks

Current model optimization procedures generally couch the uncertainties of reaction rate constants in terms of their absolute values, i.e.,  $k \pm \sigma_k$ , without regard for the method by which the value and uncertainty was obtained. The present work strongly indicates that a more sophisticated treatment of the available rate constant data, specifically including relative rate information in combustion model optimization procedures, is necessary. It is seen that this leads to a significant reduction in the allowable parameter space and, in turn, is expected to significantly affect uncertainties in model predictions of global phenomena of interest. Equally important, we suggest that the noninclusion of such information is highly likely to result in the adjustment of rate parameters such that they fall outside of a physically realistic set of values as delineated by the available experimental data or assumed rate rules. A consequence of such an omission is that “optimized” models may have less, rather than greater, fidelity to physical reality, thus raising serious questions about the ability to extrapolate such models to unstudied conditions of interest.

The above observations represent both a challenge and an opportunity for modelers, theoreticians, and experimentalists in the combustion community. The results suggest that accurate data on relative rates and product branching ratios will frequently be of greater value than measurements of absolute rate constants, at least at the current levels of measurement accuracy. We note further that computational chemistry has matured such that absolute rate constants can often be predicted with a reasonable level of accuracy. However, a number of recent comparisons of experiment and theory from this laboratory [52,55,58] have shown that the ability to accurately predict branching ratios is less well developed. This is a concern and represents an area that needs to be carefully considered, particularly for multichannel reactions that are common at high temperatures.

For experimentalists, certain types of relative rate measurements are commonly and accurately performed, for example, those involving reactions of OH with various substrates under conditions relevant to atmospheric chemistry. Data at the higher temperatures more germane to combustion are often lacking, however, and methods for such conditions need to be better developed. The atmospheric example represents relative rate measurements involving OH + RH/RH systems. Perhaps more challenging is the need to develop techniques that accurately probe unrelated reactions, e.g., H + O<sub>2</sub> versus H + RH. Such interclass comparisons are anticipated to be of great value. One can envi-

sion that the development of an accurate interlinked set of intraclass and interclass relative rate measurements will constrain models to a much greater degree than current independent measurements. Finally, for model optimizers, we suggest here that a greater emphasis on how relative rate information constrains input and output parameters is needed. While this criticism suggests some inadequacies in current implementations, we note that there is also a great deal of kinetic information that has not yet been brought to bear and we believe that its inclusion has the potential to rapidly advance the predictive capabilities of detailed kinetic models.

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