Kinetics of the Reactions of H and CH₃ Radicals with nButane: An Experimental Design Study using Reaction Network Analysis

David A. Sheen and Jeffrey A. Manion

Chemical and Biochemical Reference Data Division, National Institute of Standards and Technology, Gaithersburg, MD 20899

Abstract

The oxidation of hydrocarbon fuels proceeds through the attack of small radicals such as H and CH₃ on large molecules. These radicals abstract H atoms from the large molecules, which then usually proceed by β-scission to form C₂H₄ and C₃H₆. Quantifying these rates is critical to the development of chemical models for the oxidation of hydrocarbons. Study of this reaction system is confounded by the rapid dissociation of the intermediate radicals, which produces both additional H and additional CH₃, making it difficult to separate the behavior of the two radical species under many conditions.

In this work, we propose an experimental design algorithm that will be applied to measuring H and CH₃ attack rates on n-butane using a single-pulse shock tube. This design algorithm is based on the Method of Uncertainty Minimization using Polynomial Chaos Expansions (Sheen & Wang, Combust Flame 158, pp 2258-2374, 2011). We generate a set of proposed measurements covering a wide range of initial reactant concentrations, temperatures, and species concentration measurements. Hexamethylethane or t-butylperoxide, in mole fractions of less than 50 μL/L, generates H or CH₃ in the presence of n-butane, in mole fractions ranging from 100 μL/L to 100 000 μL/L. For some conditions, toluene was used as a radical-chain inhibitor in mole fractions of 20 000 μL/L. Temperatures ranged from 900 to 1100 K and pressures were assumed to be 2 atm. There are 16 different initial reactant concentrations and five temperatures for each concentration. For experiments using t-butylperoxide as a radical source, we consider measuring the absolute concentration of C₂H₄, C₃H₆ or measuring only the ratio between them; for hexamethylethane, we measure only the ratio, because the absolute concentrations depend on the highly-uncertain heating time. This gives a total of 160 proposed measurements.

To simulate the proposed experiments, we propose a candidate model to simulate these experiments, in this case the Jet Surrogate Fuel model. We then use a machine-learning algorithm to identify the best subset of experiments to perform. Of the original 160 conditions proposed, the algorithm selects seven as the best set. To test the machine algorithm, we compare its performance against an expert-recommended set of experimental measurements. The machine-generated experimental set performs better than the expert-generated experimental set. Therefore, the machine learning algorithm is therefore a suitable surrogate for an expert’s evaluation of a set of experiments, and can be applied to many other database analysis and constraint problems.

Key Words: shock tube, kinetics, methyl radicals, H atoms, butane, uncertainty analysis, reaction networks
1 Introduction

The oxidation of hydrocarbon fuels proceeds by means of the attack of small radicals such as H and CH$_3$ on large molecules. These radicals abstract hydrogen atoms from the large molecules, which then usually proceed by $\beta$-scission to form C$_2$H$_4$ and C$_3$H$_6$. A quantitative understanding of the radical attack process is critical to the development of chemical models for the oxidation of hydrocarbons. Furthermore, it is necessary to determine how the uncertainty in measurements used to generate the model affects the model’s final parameter estimates.

Butane is the simplest hydrocarbon that can react by H-abstraction and $\beta$-scission to form C$_2$H$_4$ and C$_3$H$_6$. It is therefore a useful subject for investigating the behavior of larger, more complex fuels. The radical (R) can attack H atoms bonded to either the primary or secondary carbon,

\[
\begin{align*}
n-C_4H_{10} + R & \leftrightarrow RH + C\cdot H_2C_3H_2 \quad \text{(primary)} \\
n-C_4H_{10} + R & \leftrightarrow RH + CH_3C\cdot HC_2H_5 \quad \text{(secondary)}
\end{align*}
\]

The $\beta$-bond for C•H$_2$C$_3H_7$ ($p$-C$_4$H$_9$) is the 2-3 bond, which upon $\beta$-scission produces ethylene and ethyl (which itself produces ethylene by H elimination). Conversely, the $\beta$-bond for CH$_3$C•HC$_2H_5$ ($s$-C$_4$H$_9$) is the 3-4 bond, which upon $\beta$-scission produces propene and methyl. In principle, then, the branching ratio for the two processes could be determined by measuring the ratio of the ethylene and propylene produced in a single-pulse shock tube.

Typically, a single-pulse shock tube study begins by the selection of a set of experimental conditions that isolates the reactions under consideration. In the case of butane, the experimental condition would be a few parts per million of a radical precursor, either hexamethyl ethane (HME) to produce H atoms or di-tert-butyl peroxide (tBPO) to produce CH$_3$ radicals, in about 2% $n$-C$_4$H$_{10}$ and 2% toluene with the balance argon. The purpose of the toluene is to act as an inhibitor for H atoms, which are eliminated from the C$_2$H$_5$ radicals and would confound measurements of CH$_3$ attack. Likewise, if the H atom pool builds too quickly in a study of H atom attack, the H atoms will begin to attack molecules other than the $n$-C$_4$H$_{10}$, producing ethylene by other pathways and thereby also confounding the measurements. Problematically, one process by which toluene inhibits the action of H atoms is by displacement of the CH$_3$ group to form benzene and a CH$_3$ radical, and so if the purpose of the experiment is to measure H atom attack on the parent fuel, some products will be produced by CH$_3$ radical attack. The measurements are further complicated by the self-combination of methyl radicals, which can produce ethylene and more H atoms.

Clearly, radical attack on saturated hydrocarbons is not sufficiently clean a system for traditional measurements. Unclean systems of this type are, however, amenable to analysis by large dataset analysis and optimization techniques such as DataCollaboration (Frenklach, Packard et al. 2004; Seiler, Frenklach et al. 2006; Russi, Packard et al. 2008) or the method of uncertainty minimization using polynomial chaos expansions (MUM-PCE) (Sheen and Wang 2011), as well as similar work by Turányi and co-workers (Turányi, Nagy et al. 2012; Zsély, Varga et al. 2012). These techniques allow a complex model such as a chemical kinetic model to be constrained against a large number of experiments, characterizing the uncertainty in the model’s parameters as a function of the
uncertainty in the experimental measurements. At their core, these methods operate using Bayes’ theorem. In the context of chemical kinetic modeling, it is usually common to talk about a candidate model $\mathcal{M}$ which is the collection of chemical and thermodynamic parameters along with their uncertainty. This model is then conditioned against a dataset $\mathcal{D}$ and an improved model is output; Bayes’ theorem can then be expressed for this system as

$$p(\mathcal{M}^*) = p(\mathcal{M}|\mathcal{D}) = \frac{p(\mathcal{D}|\mathcal{M})p(\mathcal{M}^{(0)})}{p(\mathcal{D})}$$

where $\mathcal{M}^{(0)}$ is the prior model and $\mathcal{M}^* = \mathcal{M}|\mathcal{D}$ is the improved posterior model, which has been improved by the measurements in the dataset $\mathcal{D}$.

Many chemical kinetic model optimization studies have been performed (Frenklach 1984; Yuan, Wang et al. 1991; Frenklach, Wang et al. 1992; Smith, Golden et al. 2000; Russi, Packard et al. 2008; Sheen, You et al. 2009; Sheen and Wang 2011; Sheen and Wang 2011; You, Russi et al. 2011; Turányi, Nagy et al. 2012; Zsély, Varga et al. 2012). Until very recently, however, there has not been any consideration of what comprises the best data set. When two measurements are taken independently by different researchers, it is assumed that those measurements are, in fact, statistically independent. However, the properties that are being measured are described by the same physical model, and indeed usually depend on a similar set of uncertain parameters in the model. As such, within the context of the physics that describes them, two seemingly independent measurements (say, of a laminar flame speed and of an ignition delay time) are not, in fact, independent, but are connected through the physics of the problem.

The objective of this paper is to present a machine learning algorithm that, if given a large database of experiments and a model for simulating them, is able to screen the database for redundancies and propose a new, reduced experimental database. This algorithm works by finding those experiments that have the greatest influence on a set of targeted applications. We apply the algorithm to selection of measurements of $\text{C}_2\text{H}_4$ and $\text{C}_3\text{H}_6$ in single-pulse shock tubes using mixtures of $n\text{-C}_4\text{H}_{10}$, toluene, HME and tBPO; the target applications are in this case the rate coefficients for the reactions of H abstraction by H and CH$_3$ from $n\text{-C}_4\text{H}_{10}$. The experimental dataset selected by this algorithm is compared with an expert-selected dataset and found to constrain the application rate coefficients generally better than the choices of the expert.

2 Methodology

2.1 Prior Model

The prior model, denoted $\mathcal{M}^{(0)}$, is the submodel for the oxidation of H$_2$, CO, and C$_1$-C$_4$ hydrocarbons from JetSurF 2, augmented as described in (Sheen, Rosado-Reyes et al. 2013). Rate constants are specified using a modified Arrhenius expression $k_n = A_n T^{b_n} \exp(E_n/T)$. 

3
2.2 Application Dataset

Since the objective of the measurements is to determine the rate constants for radical attack on \(n\)-\(C_4H_{10}\), the applications are the Arrhenius prefactors and activation energies for the reactions,

\[
\begin{align*}
  n\text{-}C_4H_{10} + H & \leftrightarrow H_2 + p\text{-}C_4H_9 \quad \text{R633} \\
  n\text{-}C_4H_{10} + H & \leftrightarrow H_2 + s\text{-}C_4H_9 \quad \text{R634} \\
  n\text{-}C_4H_{10} + CH_3 & \leftrightarrow CH_4 + p\text{-}C_4H_9 \quad \text{R643} \\
  n\text{-}C_4H_{10} + CH_3 & \leftrightarrow CH_4 + s\text{-}C_4H_9 \quad \text{R644}
\end{align*}
\]

The application set \(\mathcal{A}\) then consists of the Arrhenius prefactors \(A_{633}, A_{634}, A_{643}\) and \(A_{644}\), the activation energies \(E_{633}, E_{644}, E_{643}\), and \(E_{644}\), as well as the ratios \(A_{633}/A_{634}\) and \(A_{643}/A_{644}\), and the differences \(E_{633} – E_{644}\) and \(E_{643} – E_{644}\).

2.3 Experimental Dataset

The experimental measurements consist of measurements of \(C_2H_4\) and \(C_3H_6\) in mixtures of varying concentrations of \(n\)-\(C_4H_{10}\) and toluene, using HME or \(t\)BPO as a source of H or CH\(_3\) radicals. The complete list of experiments is given in Table 1. In order to validate the experimental selection method, we consulted an outside expert to generate a dataset, denoted \(\mathcal{D}_{\text{expert}}\). The expert suggested [W. Tsang, personal communication] that the experiments should be conducted with large excesses of toluene and butane, so this set consists of Experiments 1, 5, 6, 10, 125, and 130.

Mathematically, we characterize each measurement as a dataset element \(\mathcal{D}_r\) so that the dataset \(\mathcal{D} = \bigcup_r \mathcal{D}_r\), with \(\bigcup_r\) denoting the union operator. Each \(\mathcal{D}_r\) is described by a measurement value \(\eta_r^{\text{obs}}\) and a measurement uncertainty \(\sigma_r^{\text{obs}}\), in addition to metadata such as composition, geometry, etc. Since the experiments have not yet been done, we take \(\eta_r^{\text{obs}}\) to be the same as the prior model’s prediction and we assume a reasonable value for \(\sigma_r^{\text{obs}}\), in this case 0.05 in the logarithm, equivalent to a 2\(\sigma\) uncertainty of 10\%. Active parameters are determined in the same manner as (Sheen, Rosado-Reyes et al. 2013); briefly, For each experiment \(\mathcal{D}_r\) and reaction rate parameter \(\theta_i\) (either an Arrhenius prefactor or activation energy), the uncertainty-weighted sensitivity coefficient \(S_{i,k}\) was computed,

\[
S_{r,i} = \frac{d\eta_r}{d\theta_i} \frac{\theta_i}{\eta_r} \ln f_i
\]

where \(\eta_r\) is the simulation prediction, \(\theta_i\) is a generalized rate parameter and \(f_i\) is its uncertainty factor. The active rate parameters are those for which \(S_{r,i}/S_{r,\text{max}} > 0.02\). Uncertainty factors in the Arrhenius prefactors are taken from JetSurF 2 (Wang, Dames et al. 2010). Uncertainty factors in activation energies where estimated using \(f_i = (E_k + T_c \ln F_k)/E_k\), where \(E_k\) is the activation energy of \(R_k\) and \(F_k\) is the uncertainty factor of \(R_k\), with \(T_c = 1000\) K. This formulation ensures that the activation energy contributes the same uncertainty to the rate constant as the Arrhenius prefactor at 1000 K. In simulations, the shock tube was treated as a homogeneous adiabatic reactor. Species
concentrations following the shock were determined used the VODE solver (Brown, Byrne et al. 1989) to integrate the chemical rate equations supplied by Sandia CHEMKIN (Kee, Rupley et al. 1989) over a period of 500 µs. There are 25 active reactions and 44 active parameters, which are given in Table 2.

2.4 Model Constraint

Model constraint uses the method of uncertainty analysis using polynomial chaos expansions (MUM-PCE) (Sheen and Wang 2011). This is a method for finding the best set of rate parameters for a given set of experimental measurements. A prior model $\mathcal{M}^{(0)}$ is defined, and then conditioned against a set of experimental data $\mathcal{D}$, thus generating a posterior model $\mathcal{M}^*$, or, in probabilistic terms, $\mathcal{M}^* = \mathcal{M}\mid(\mathcal{D}, \mathcal{M}^{(0)})$. It is assumed that the uncertain parameters in the model can be expressed as a vector $\mathbf{x} = \mathbf{x}^{(0)} + \mathbf{x}^{(1)}\xi$, where $\mathbf{x}^{(0)}$ is the factorial variable vector whose elements are

$$x_i^{(0)} = \frac{\ln \theta_i/\theta_i^{0}}{\ln f_i} \quad (2)$$

where $f_i$ is the uncertainty factor of the $i^{th}$ generalized active parameter $\theta_i$. $\xi$ is a vector of independent, identically distributed normal random variables with mean 0 and variance 1, and $\mathbf{x}^{(1)}$ is a transformation matrix, so that $\mathbf{X}$ follows a multivariate normal distribution with mean $\mathbf{x}^{(0)}$ and covariance matrix $\Sigma = \mathbf{x}^{(1)}\mathbf{x}^{(1)T}$. $\mathcal{M}^{(0)}$ assumes $\mathbf{x}^{(0)} = 0$ and $\mathbf{x}^{(1)}$ equal to one-half times the identity matrix. This is equivalent to each rate coefficient being lognormally distributed about its nominal value with a 2σ uncertainty equal to its uncertainty factor. The rate parameters for the posterior model can then be estimated using Bayes’ Theorem, which yields the following expression for the probability density function (PDF) of the rate parameters,

$$\ln P_\mathbf{x}(\mathbf{x}) \sim -\left[\sum_{r=1}^{N_e} \left(\frac{\eta_r(\mathbf{x}) - \eta_r^{obs}}{\sigma_r^{obs}}\right)^2 + \sum_{i=1}^{N_r} 4x_i^2\right] \quad (3)$$

where $\eta_r(\mathbf{x})$ is the model prediction of $\mathcal{D}_r$ as a function of the factorial variables $\mathbf{x}$, $N_e$ is the number of experiments and $N_r$ the number of active variables. This PDF is then approximated by a multivariate normal distribution with some $\mathbf{x}^{(0)*}$ and some $\Sigma^*$. $\mathbf{x}^{(0)*}$ is found by finding the mode of the PDF in Eq. 3, equivalent to the least-squares optimization problem

$$\mathbf{x}^{(0)*} = \operatorname*{argmax}_{\mathbf{x}} \ln P_\mathbf{x}(\mathbf{x}) \quad (4)$$

which is solved using the LMDIF solver in the MINPACK library (More, Garbow et al. 1999). $\Sigma^*$ is found by linearizing the model predictions in the vicinity of $\mathbf{x}^{(0)*}$, which yields
\[ \Sigma^* = \left( \sum_{r=1}^{N_e} \frac{J_r J_r^T}{(\sigma_r^{obs})^2} + 4I \right)^{-1} \]  

(5)

where \( J_r \) is the gradient of \( \eta_r(x^{(0)*}) \). Solution mapping (Frenklach 1984; Frenklach, Wang et al. 1992) is used to estimate the model predictions, which assumes that \( \eta_r(X) = X^T b_r X + a_r^T X + \eta_0 \), where \( a_r \) and \( b_r \) are expansion coefficients, calculated using the sensitivity-analysis-based method (SAB) (Davis, Mhadeshwar et al. 2004). Then \( J_r \) in Eq. 5 is \( J_r = 2b_r x^{(0)*} + a_r \).

### 2.5 Experimental Discrimination

The form of Eq. 2 assumes that \( p(D|M) = \prod_r p(D_r|M) \), equivalent to saying that all of the experimental measurements are independent. This is not guaranteed or in fact very likely at all. A method such as DataCollaboration, because it assumes that the probability distributions are what is called an interval distribution, does not have this concern. However, interval distributions do not use a probabilistic interpretation, which some researchers have found to be problematic. Statistical methods such as MUM-PCE (Sheen and Wang 2011) and those employed by Turanyi and co-workers (Turányi, Nagy et al. 2012), on the other hand, are inherently probabilistic, but are therefore highly susceptible to over-constraining the data set by including many non-independent measurements.

If two measurements are not independent, we must figure out how to address this non-independence. The work of Turanyi and co-workers (Turányi, Nagy et al. 2012) uses a “size of the dataset” measure to normalize O(20,000) individual measurements of a species time history in the shock-tube oxidation of \( H_2 \) in \( O_2 \). This assumes that all of the measurements within a particular subset are equally correlated (and are independent of measurements outside that data subset), which might not be true. The algorithm proposed here addresses this question by finding the “most independent” set of experiments.

The amount of information provided by a particular experiment about a simulation can be estimated by the sensitivity \( S_H \) of the simulation’s uncertainty to the measurement uncertainty, which can be expressed as

\[ S_{H,ij} = \frac{d \sigma_{j*}}{d \sigma_{i}^{obs}} \frac{\sigma_{i}^{obs}}{\sigma_{j*}} \]  

(6)

where \( \sigma_{i}^{obs} \) is the uncertainty in the \( i^{th} \) experimental measurement and \( \sigma_{j*} \) is the posterior uncertainty in the \( j^{th} \) simulation prediction. \( S_{H,ij} \) is essentially the derivative of the entropy \( H \) of the simulation to that of the experimental measurement and it provides an estimate of how an incremental improvement in the measurement precision affects the simulation uncertainty, which gives an estimate of how important that experiment is with respect to the simulation under consideration. If \( S_H \) is cast as a matrix, then examining column \( i \) gives a measure of how much information is coming from experiment \( i \) into the simulations, while examining row \( j \) gives a
measure of how much information is coming from the experiments into simulation $j$. A net information flux $\Phi_r$ can be defined as

$$\Phi_r = (S_H^T S_H - S_H S_H^T)_{rr} = \sum_{j=1}^{M} (S_{H,rj}^2 - S_{H,jr}^2)$$

which is an estimate of the aggregate information coming into or out of an experiment. $D^*$ is determined by the following method. $\Phi_r$ is calculated for each experiment, with uncertainties calculated by means of the method of uncertainty minimization using polynomial chaos expansions (MUM-PCE) (Sheen and Wang 2011). If any $D_r$ has $\Phi_r < 0$, the one with the smallest value is removed from the experimental list and new values of $\Phi_r$ are calculated. This procedure is iterated until all remaining $D_r$ have $\Phi_r > 0$. It should be noted that removed targets are not considered as applications; they are removed from consideration entirely. Additionally, it can be shown that, as the experimental uncertainty of a particular target, $\sigma_i^{obs}$ gets smaller, its self-entropy derivative $S_{H,ii}$ approaches 1; this makes sense because the model uncertainty is now locked to the experimental uncertainty. However, at the same time, the other entropy derivatives $S_{H,ij}$ approach 0; in this case, simulations of other experiments depend on some chemistry that is not constrained by this experiment.

Examination of $\Phi_r$ reveals that $\sum_r \Phi_r = 0$, so that with each iteration approximately half of the members of $D \cup A$ will have $\Phi_r < 0$ and thus be eligible for removal. The presence of the application set $A$, whose members must have $\Phi_r < 0$ because there is no measurement information about them, serves to increase $\Phi_r$ for the members of $D$. This is a rigorous statement of the critical need for an experimental study to be performed with an application in mind; it does not make sense to simply do experiments in a vacuum. It is intuitively obvious that an application is necessary, but that it is an emergent property serves as a validation of the information flux selection criterion.

3 Results and Discussion

As can be seen in Table 2, the number of active reactions is much greater than four. For instance, the $C_2H_4$ concentration is strongly affected by R108 and R252,

$$\begin{align*}
2\text{CH}_3 &\leftrightarrow \text{H} + \text{C}_2\text{H}_5 & \quad \text{R108} \\
\text{C}_2\text{H}_4 + \text{H}(+\text{M}) &\leftrightarrow \text{C}_2\text{H}_5(+\text{M}) & \quad \text{R252}
\end{align*}$$

The rates of H atom attack on toluene also affect the $C_2H_4$ concentration, toluene’s purpose being to remove the H atoms before they can attack the $n$-$C_4H_{10}$. As expected, the system is not very clean, and would not be expected to be easily scrutinized by traditional methods, hence our desire to find which conditions give the most knowledge about this highly unclean system.

The entropy sensitivity matrix, $S_H$, is presented in Fig. 1 for $D^{(0)}$. Many of the measurement conditions are strongly correlated, as indicated by the large off-diagonal values of $S_H$ and the comparatively small diagonal values. Furthermore, the correlations among the experiments under
different conditions, for instance measurements of H attack and CH₃ attack, underscore how unclean
the system is. However, they also indicate the possibility of finding a set of conditions that will
effectively span the reaction rate space of interest.

Entropy sensitivity can be thought of as a kind of information flow, indicating how much a
particular experiment tells about a particular simulation. The information flux Φᵣ is then essentially
a measure of the integrated information flux for a particular experiment. If this number is positive,
then the rᵗʰ experiment provides more information about simulating other experiments than the other
experiments provide about simulating it, and conversely if Φᵣ is negative then other experiments
provide more information about simulating the rᵗʰ experiment. The presence of application
experiments is critical because two targets will always be coupled, that is, each will provide some
information about simulating the others. In the limiting case of two targets and no applications, the
information flux criterion will always eliminate one. Hence the application is critical to informing
which measurements are the important ones.

In order to determine which experiments should be removed from consideration, the information
flux Φᵣ is calculated and presented in Fig. 2. It averages to 0 and so about half of the experiments
are eligible for removal. The target with the lowest Φᵣ is removed and the information flux recalculated until every target has a positive Φᵣ. After the last iteration, six experiments remain, and
their experimental conditions are listed in Table 3. Sₜ for the final iteration is presented in Fig. 3.
Ideally, Sₜ would be diagonal, which would mean that there was very little cross-coupling among
the members of D⁺; in reality it deviates from this ideal state, but it can be seen that the diagonals are
much larger in the case of D than D⁰.

Once the final experimental list is determined, it could be asked whether this is actually the best
set of experiments. To address this question, the uncertainties of the applications are presented in
Table 4. The uncertainty of the reaction A factors is typically about 0.6 (compared to 1 for the prior
model). The uncertainty of the activation energies is about 0.9, which is expected since the
temperature range of the experiments is relatively small (900 K – 1100 K).

The information flux criterion selected seven experiments from the full set of 160. One question,
then, is why these particular experiments were picked, given that many of the experiments are so
similar. Another distressing result can be seen in Fig. 4, which shows the posterior uncertainties for
all of the experiments. Many experiments have posterior uncertainties larger than 10%, which
suggests that we would learn more about the model if we included these experiments, e.g.
experiments 91-95. What is it, then, about these seven experiments that makes them the best?

We begin by compiling the expert-suggested dataset, D_{expert}, which consists of six
measurements, which are 10% n-butane, 2% toluene, and 50 parts per million HME or tBPO, at 900
and 1100 K. The uncertainties in A are tabulated in Table 4. The uncertainties for A₆₄₃ and A₆₄₄ are
similar to (or slightly less than) those calculated using D⁺, but the uncertainties in A₆₃₃ and A₆₃₄ are
much less in the case of D⁺ than for D_{expert}, so the information flux algorithm can outperform the
expert.

Some properties of D⁺ are obvious. For instance, in the experiments involving CH₃ attack on n-
C₄H₁₀, (mixtures of n-C₄H₁₀ and tBPO), measurements of [C₂H₄]/[C₃H₆] and of absolute [C₃H₆] are
suggested, while measurements of absolute \([C_2H_4]\) are contra-indicated. Obviously, these three values are related, and only two of them need be independently specified. It is not obvious why \([C_2H_4]\) measurements are not included. To demonstrate this, we show in Fig. 5 the joint density functions of \(A_{643}\) and \(A_{644}\) for two cases, one where the reaction rates are constrained against the absolute \([C_2H_4]\) and \([C_3H_6]\) and one where the reaction rates are constrained against \([C_2H_4]/[C_3H_6]\) and \([C_3H_6]\). It is impossible to see any difference in the figure; the joint density is slightly smaller in the latter case.

The information flux algorithm chose targets that predominantly have a low concentration of \(n\)-\(C_4H_{10}\), contrary to the expert-selected data set. To explain why, we first examine how the uncertainty of the rate parameters for R643 and R644 changes depending on which measurements we choose to constrain the system. The marginal joint density function of \(A_{643}\) and \(A_{644}\) is shown in Fig. 6 as a function of the initial \(n\)-\(C_4H_{10}\) mole fraction when the system is constrained against measurements in mixtures of \(n\)-\(C_4H_{10}\) and \(tBPO\). At an initial mole fraction of 0.01%, the lowest considered, the posterior uncertainty in \(A_{643}\) is the same as the prior value; there is no information about the rate of R643. When the initial mole fraction is increased to 0.1%, the uncertainty in \(A_{643}\) is reduced to 60% of its prior value. As the initial \(n\)-\(C_4H_{10}\) mole fraction is increased further, there is little change in the joint density function of \(A_{643}\) and \(A_{644}\).

To address why there is so little information about \(A_{643}\) at low mole fractions of \(n\)-\(C_4H_{10}\), we show in Fig. 7. the marginal joint densities of \(A_{643}\) and \(A_{108}\) as a function of initial \(n\)-\(C_4H_{10}\) mole fraction. At 10%, there is no information about \(A_{108}\), while \(A_{643}\) is strongly constrained. As the initial \(n\)-\(C_4H_{10}\) mole fraction is decreased, the uncertainty in the product \(A_{643}A_{108}\) (as evidenced by the PDF’s extend in the \(y = x\) direction) is reduced at the expense of more uncertainty in the value of \(A_{643}\) (proportional to the ellipse’s extent along the \(x\)-axis). Somewhere between a 0.1% and 0.01% initial \(n\)-\(C_4H_{10}\) mole fraction, there is a transition and \(A_{108}\) becomes strongly constrained, with very little information about \(A_{643}\), similar to what was shown in Fig. 3. In these experiments, the thermal decomposition of \(tBPO\) very rapidly forms a large number of \(CH_3\) radicals, and if \([n\)-\(C_4H_{10}\]\) is comparable to \([CH_3]\), they are more likely to recombine with each other via R108 than to attack \(n\)-\(C_4H_{10}\) via R643 and R644. Most of the measured ethylene is formed through R108 rather than through R644, so measurements at low \(n\)-\(C_4H_{10}\) mole fractions are really measuring the rate of R108.

However, as the initial \(n\)-\(C_4H_{10}\) mole fraction is increased, more \(H\) atoms are formed through R644. When the initial \(n\)-\(C_4H_{10}\) mole fraction is 10%, \(H\) atoms are formed in sufficient quantity that a substantial amount of \(C_2H_4\) and \(C_3H_6\) comes from \(H\) attack rather than \(CH_3\) attack. The joint density function of \(A_{633}\) and \(A_{634}\) is shown in Fig. 8. At 0.1%, there is no information about these parameters, whereas at 10%, the uncertainty in \(A_{633}/A_{634}\) (the extent of the ellipse in the \(y = -x\) direction) is constrained fairly strongly.

Figures 6 and 8 indicate that measuring \([C_2H_4]\) and \([C_3H_6]\) in a mixture of 10% \(n\)-\(C_4H_{10}\) and \(tBPO\) could provide a simultaneous measurement of all the title reactions, R633, R634, R643, and R644. This would seem to indicate that we can measure the \(CH_3\) and \(H\) atom attack process simply with this one set of experiments. The information flux algorithm did not pick these experiments to measure \(A_{633}/A_{634}\), however. In Fig. 9, we show the joint density function for \(A_{633}\) and \(A_{634}\), as
constrained by the $[\text{C}_2\text{H}_4]/[\text{C}_3\text{H}_6]$ measurements in mixtures of $n$-$\text{C}_4\text{H}_{10}$ and HME. For mixtures of 10% $n$-$\text{C}_4\text{H}_{10}$ and HME, $A_{633}/A_{634}$ is constrained about as well as it is by mixtures of 10% $n$-$\text{C}_4\text{H}_{10}$ and tBPO. As the initial mole fraction is decreased, the uncertainty in $A_{633}/A_{634}$ (the extent of the ellipse in the $y = -x$ direction) becomes smaller until 0.1% $n$-$\text{C}_4\text{H}_{10}$, after which it stops decreasing.

Toluene is used as an H-atom inhibitor. In experiments using tBPO, its purpose is to convert H atoms into CH$_3$ radicals via R674, thus reducing the confounding effect from H attack, which is almost 1000 times faster. In experiments using HME, the purpose is to reduce the H atom attack rate on butane by reducing the size of the H pool; the pool of CH$_3$ radicals never grows very large, so the confounding effect from CH3 attack is small, especially at low initial $n$-$\text{C}_4\text{H}_{10}$ mole fractions. The question, then, what effect the toluene has on the measurements of the title rates. In Fig. 10, we present the joint density function for $A_{633}$ and $A_{634}$, as in Fig. 6, except using toluene as a radical inhibitor. For fixed initial $n$-$\text{C}_4\text{H}_{10}$ mole fraction, the uncertainty in $A_{633}/A_{634}$ is slightly greater when toluene is used, although the effect is not easy to see in the figure.

The selection of 10% and 1% $n$-$\text{C}_4\text{H}_{10}$ and tBPO represents a compromise. On the one hand, there is the desire to minimize the overlap between the H attack and CH$_3$ attack measurements, because two experiments measuring the same thing is bad; this requires low initial $n$-$\text{C}_4\text{H}_{10}$. On the other hand, for low initial $n$-$\text{C}_4\text{H}_{10}$, so much ethylene comes from R108 that $A_{643}$ cannot be measured. Making measurements at an initial mole fraction of 1% $n$-$\text{C}_4\text{H}_{10}$ and tBPO minimizes both of these effects. Conversely, experiments with 0.1% and 0.01% $n$-$\text{C}_4\text{H}_{10}$ and HME are selected because there is no loss of information at low butane concentrations, but at high butane concentrations there is significant CH$_3$ production and therefore product formation through the CH$_3$ attack pathways.

Some selections are somewhat random. Experiments using HME and toluene are selected even though Fig. 10 suggests that these are not good experiments to choose. To see how important these experiments really are, we remove experiments with both HME and toluene and generate a new dataset, $D^{+}$. The uncertainties in the reaction rate coefficients are shown in Table 4, and the uncertainties in $D^{+}$ are essentially the same as those in $D^{*}$. This means that the “objective function” being minimized by the algorithm, namely the uncertainty in the targeted rate parameters, is relatively flat, so that some fairly large motions within the experimental condition space are possible without changing the final rate parameter uncertainty. Whatever $D^{*}$ the algorithm generates is therefore not unique; rather, the algorithm is presenting guidelines for how to select experimental measurements based on the initial dataset $D^{(0)}$ that it was given as input.

4 Conclusion

A machine-learning algorithm was developed to determine a minimal set of experiments for constraining a model based on minimizing the uncertainty in the model’s predictions of a set of applications. This algorithm was applied to measuring the rates of H-atom and methyl radical attack on normal butane. A candidate data set of 160 experimental conditions was compiled, and the algorithm chose seven conditions from this set. When the experimental set chosen by the algorithm was compared with an expert-selected set, it was found that the set chosen by the algorithm differed substantially from the expert-selected data set. In particular, the expert-selected set prefers large
amounts of butane (several percent), whereas the algorithm generally preferred smaller amounts (0.1%). When the uncertainty in the applications resulting from using the algorithm-generated as opposed to the expert-selected data sets, it was found that the algorithm compared reasonably well at constraining the uncertainties in the rate constants of methyl radical attack, and better constrained the rate constants of H-atom attack than the expert-selected set. The machine-learning algorithm proposed here is, therefore, a reasonable surrogate for expert database analysis and evaluation and, although demonstrated here in the context of chemical kinetics, has potentially wide-reaching applications.

References


### Tables

Table 1. Experimental conditions in the initial dataset $\mathcal{D}^{(0)}$.

Composition (mole fraction)

<table>
<thead>
<tr>
<th>$\text{C}<em>4\text{H}</em>{10}$</th>
<th>Toluene</th>
<th>Precursor</th>
<th>Precursor</th>
<th>$r^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-1}$</td>
<td>0.02</td>
<td>$5 \times 10^{-5}$</td>
<td>tBPO</td>
<td>1.5 $^a$; 6-10 $^b$; 11-15 $^c$</td>
</tr>
<tr>
<td>$10^{-1}$</td>
<td>0.02</td>
<td>$2.5 \times 10^{-5}$</td>
<td>tBPO</td>
<td>16-20; 21-25; 26-30</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>0.02</td>
<td>$5 \times 10^{-5}$</td>
<td>tBPO</td>
<td>31-35; 36-40; 41-45</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>0.02</td>
<td>$2.5 \times 10^{-5}$</td>
<td>tBPO</td>
<td>46-50; 51-55; 56-60</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>0.02</td>
<td>$5 \times 10^{-5}$</td>
<td>tBPO</td>
<td>61-65; 66-70; 71-75</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>0.02</td>
<td>$2.5 \times 10^{-5}$</td>
<td>tBPO</td>
<td>76-80; 81-85; 86-90</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>0.02</td>
<td>$5 \times 10^{-5}$</td>
<td>tBPO</td>
<td>91-95; 96-100; 101-105</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>0.02</td>
<td>$2.5 \times 10^{-5}$</td>
<td>tBPO</td>
<td>106-110; 111-115; 116-120</td>
</tr>
<tr>
<td>$10^{-1}$</td>
<td>0</td>
<td>$5 \times 10^{-5}$</td>
<td>HME</td>
<td>121-125 $^c$</td>
</tr>
<tr>
<td>$10^{-1}$</td>
<td>0.02</td>
<td>$5 \times 10^{-5}$</td>
<td>HME</td>
<td>126-130</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>0</td>
<td>$5 \times 10^{-5}$</td>
<td>HME</td>
<td>131-135</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>0.02</td>
<td>$5 \times 10^{-5}$</td>
<td>HME</td>
<td>136-140</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>0</td>
<td>$5 \times 10^{-5}$</td>
<td>HME</td>
<td>141-145</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>0.02</td>
<td>$5 \times 10^{-5}$</td>
<td>HME</td>
<td>146-150</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>0</td>
<td>$5 \times 10^{-5}$</td>
<td>HME</td>
<td>151-155</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>0.02</td>
<td>$5 \times 10^{-5}$</td>
<td>HME</td>
<td>156-160</td>
</tr>
</tbody>
</table>

a. Measuring $[\text{C}_2\text{H}_4]$; b. Measuring $[\text{C}_3\text{H}_6]$; c. Measuring $[\text{C}_2\text{H}_4]/[\text{C}_3\text{H}_6]$; d. Five measurements at 50 K intervals from $T_5 = 900$ K to 1100 K.
Table 2. List of active rate coefficients and uncertainty factors. The title reactions are in bold.

<table>
<thead>
<tr>
<th>n</th>
<th>Title Reactions</th>
<th>A</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>633</td>
<td>$C_4H_{10} + H \rightarrow p-C_4H_9 + H_2$</td>
<td>18 3</td>
<td>38 1.2</td>
</tr>
<tr>
<td>634</td>
<td>$C_4H_{10} + H \rightarrow s-C_4H_9 + H_2$</td>
<td>19 3</td>
<td>39 1.2</td>
</tr>
<tr>
<td>643</td>
<td>$C_4H_{10} + CH_3 \rightarrow p-C_4H_9 + CH_4$</td>
<td>20 3</td>
<td>40 1.2</td>
</tr>
<tr>
<td>644</td>
<td>$C_4H_{10} + CH_3 \rightarrow s-C_4H_9 + CH_4$</td>
<td>21 3</td>
<td>41 1.2</td>
</tr>
<tr>
<td>107</td>
<td>$2CH_3(+M) \rightarrow C_2H_6(+M)$</td>
<td>1 2</td>
<td>26 1.2</td>
</tr>
<tr>
<td>108</td>
<td>$2CH_3 \rightarrow H + C_2H_5$</td>
<td>2 5</td>
<td>27 1.2</td>
</tr>
<tr>
<td>131</td>
<td>$CH_4 + CH_2 \rightarrow 2CH_3$</td>
<td>3 5</td>
<td>-</td>
</tr>
<tr>
<td>252</td>
<td>$C_6H_5 + H(+M) \rightarrow C_6H_4(+M)$</td>
<td>4 3</td>
<td>28 1.2</td>
</tr>
<tr>
<td>279</td>
<td>$C_2H_5 + CH_3(+M) \rightarrow C_2H_4(+M)$</td>
<td>5 3</td>
<td>-</td>
</tr>
<tr>
<td>286</td>
<td>$C_2H_5 + CH_3 \rightarrow C_2H_4 + CH_4$</td>
<td>6 1.5</td>
<td>29 1.08</td>
</tr>
<tr>
<td>362</td>
<td>$C_2H_5 + H \rightarrow C_2H_4 + CH_3$</td>
<td>7 2</td>
<td>30 1.12</td>
</tr>
<tr>
<td>554</td>
<td>$1-C_4H_8 + H(+M) \rightarrow C_4H_7(+M)$</td>
<td>8 3</td>
<td>31 1.2</td>
</tr>
<tr>
<td>555</td>
<td>$1-C_4H_8 + H \rightarrow C_2H_4 + C_2H_5$</td>
<td>9 3</td>
<td>32 1.2</td>
</tr>
<tr>
<td>556</td>
<td>$1-C_4H_8 + H \rightarrow C_3H_6 + CH_3$</td>
<td>10 5</td>
<td>33 1.2</td>
</tr>
<tr>
<td>565</td>
<td>$2-C_4H_8 + H(+M) \rightarrow C_2H_6(+M)$</td>
<td>11 3</td>
<td>34 1.2</td>
</tr>
<tr>
<td>573</td>
<td>$i-C_4H_8 + H \rightarrow i-C_3H_7 + H_2$</td>
<td>12 3</td>
<td>-</td>
</tr>
<tr>
<td>574</td>
<td>$i-C_4H_8 + H \rightarrow i-C_3H_6 + CH_3$</td>
<td>13 3</td>
<td>35 1.2</td>
</tr>
<tr>
<td>582</td>
<td>$C_2H_5 + C_2H_5 \rightarrow C_6H_7$</td>
<td>14 3</td>
<td>36 1.2</td>
</tr>
<tr>
<td>592</td>
<td>$C_3H_6 + CH_3(+M) \rightarrow C_4H_9(+M)$</td>
<td>15 2</td>
<td>37 1.19</td>
</tr>
<tr>
<td>631</td>
<td>$nC_4H_11(+M) \rightarrow C_4H_{10}(+M)$</td>
<td>16 2</td>
<td>-</td>
</tr>
<tr>
<td>632</td>
<td>$2C_2H_5(+M) \rightarrow C_4H_{10}(+M)$</td>
<td>17 2</td>
<td>-</td>
</tr>
<tr>
<td>673</td>
<td>$C_6H_5 + CH_3 \rightarrow C_6H_4 + CH_2 + H_2$</td>
<td>22 2</td>
<td>42 1.16</td>
</tr>
<tr>
<td>674</td>
<td>$C_2H_5 + CH_3 \rightarrow C_6H_4 + CH_2$</td>
<td>23 2</td>
<td>43 1.2</td>
</tr>
<tr>
<td>676</td>
<td>$C_2H_5 + CH_3 \rightarrow C_6H_4 + CH_2 + CH_4$</td>
<td>24 2</td>
<td>44 1.14</td>
</tr>
<tr>
<td>805</td>
<td>$C_2H_5 + CH_3 \rightarrow C_6H_4 C_2H_3$</td>
<td>25 2</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 3. Experimental conditions in the final datasets $\mathcal{D}^*$ and $\mathcal{D}^{*\dagger}$.

<table>
<thead>
<tr>
<th>Composition (Mole fraction)</th>
<th>Final dataset $\mathcal{D}^*$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$i^*$</td>
<td>$i$</td>
<td>$C_4H_{10}$ Toluene</td>
</tr>
<tr>
<td>1</td>
<td>6</td>
<td>$10^{-1}$</td>
</tr>
<tr>
<td>2</td>
<td>86</td>
<td>$10^{-3}$</td>
</tr>
<tr>
<td>3</td>
<td>89</td>
<td>$10^{-3}$</td>
</tr>
<tr>
<td>4</td>
<td>96</td>
<td>$10^{-4}$</td>
</tr>
<tr>
<td>5</td>
<td>145</td>
<td>$10^{-3}$</td>
</tr>
<tr>
<td>6</td>
<td>150</td>
<td>$10^{-3}$</td>
</tr>
<tr>
<td>7</td>
<td>156</td>
<td>$10^{-4}$</td>
</tr>
</tbody>
</table>

Table 4. Uncertainty in the applications $\mathcal{A}$ ($A$ factors, activation energies $E$, and the parameter ratio) expressed as $\sigma^{(0)}/\sigma$ for the final datasets, $\mathcal{D}^*$ and $\mathcal{D}^{*\dagger}$, and the expert dataset $\mathcal{D}^{\text{expert}}$. If the uncertainty in an application is less than the corresponding value in $\mathcal{D}^*$, the entry is shown in bold italics.

<table>
<thead>
<tr>
<th>$\mathcal{D}^*$</th>
<th>R633</th>
<th>R634</th>
<th>R643</th>
<th>R644</th>
<th>$A_{633}$/$A_{634}$</th>
<th>$E_{633}$/$E_{634}$</th>
<th>$A_{643}$/$A_{644}$</th>
<th>$E_{643}$/$E_{644}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>0.66</td>
<td>0.86</td>
<td>0.62</td>
<td>0.92</td>
<td>0.92</td>
<td>0.64</td>
<td>0.64</td>
<td>0.84</td>
</tr>
<tr>
<td>$E$</td>
<td>0.66</td>
<td>0.82</td>
<td>0.62</td>
<td>0.92</td>
<td>0.92</td>
<td>0.64</td>
<td>0.64</td>
<td>0.84</td>
</tr>
<tr>
<td>$\mathcal{D}^{*\dagger}$</td>
<td>R633</td>
<td>R634</td>
<td>R643</td>
<td>R644</td>
<td>$A_{633}$/$A_{634}$</td>
<td>$E_{633}$/$E_{634}$</td>
<td>$A_{643}$/$A_{644}$</td>
<td>$E_{643}$/$E_{644}$</td>
</tr>
<tr>
<td>$A$</td>
<td>0.66</td>
<td>0.82</td>
<td>0.62</td>
<td>0.92</td>
<td>0.92</td>
<td>0.64</td>
<td>0.64</td>
<td>0.84</td>
</tr>
<tr>
<td>$E$</td>
<td>0.66</td>
<td>0.82</td>
<td>0.62</td>
<td>0.92</td>
<td>0.92</td>
<td>0.64</td>
<td>0.64</td>
<td>0.84</td>
</tr>
<tr>
<td>$\mathcal{D}^{\text{expert}}$</td>
<td>R633</td>
<td>R634</td>
<td>R643</td>
<td>R644</td>
<td>$A_{633}$/$A_{634}$</td>
<td>$E_{633}$/$E_{634}$</td>
<td>$A_{643}$/$A_{644}$</td>
<td>$E_{643}$/$E_{644}$</td>
</tr>
<tr>
<td>$A$</td>
<td>0.80</td>
<td>0.94</td>
<td>0.72</td>
<td>0.96</td>
<td>0.60</td>
<td>0.84</td>
<td>0.84</td>
<td>0.88</td>
</tr>
<tr>
<td>$E$</td>
<td>0.80</td>
<td>0.94</td>
<td>0.72</td>
<td>0.96</td>
<td>0.60</td>
<td>0.84</td>
<td>0.84</td>
<td>0.88</td>
</tr>
</tbody>
</table>
Figure 1. Entropy derivative matrix $S_{ii}$ for the experimental dataset $\mathcal{D}^{(0)}$ and application dataset $\mathcal{A}$. Values of $i$ and $j$ between 1 and 160 refer to experiments in $\mathcal{D}^{(0)}$; see Table 1 for index numbers. Values of $i$ and $j$ greater than 160 refer to the $A$-factors and activation energies in $\mathcal{A}$. Color indicates the value of $S_{ii}$.\vspace{0.5cm}
Figure 2. Information flux $\Phi_i$ for the experiments in $\mathcal{D}^{(0)}$. Values of $i$ and $j$ between 1 and 160 refer to experiments in $\mathcal{D}^{(0)}$; see Table 1 for index numbers. Values of $i$ and $j$ greater than 160 refer to the A-factors and activation energies in $\mathcal{A}$. See Table 1 for index numbers.
Figure 3. Entropy derivative matrix $S_{ij}$ for the experimental dataset $D^*$ and application dataset $A$. Values of $i^*$ and $j^*$ between 1 and 7 refer to experiments in $D^*$; see Table 3 for index numbers. Values of $i^*$ and $j^*$ greater than 7 refer to the A-factors and activation energies in $A$. Color indicates the value of $S_{ij}$. 
Figure 4. Posterior uncertainty for $M^*|D^*$. The experimental uncertainty of 0.05 is marked with the heavy black line. See Table 1 for index numbers.
Figure 5. Joint probability density functions of the factorial variables corresponding to $A_{434}$ and $A_{444}$. Concentric circles are the PDFs of the prior model. Concentric ellipses are the PDFs of the posterior models (left) considering measurements of absolute $[C_2H_4]$ and $[C_3H_6]$ and (right) considering measurements of absolute $[C_3H_4]$ and $[C_2H_4]/[C_3H_6]$. The initial $[n-C_4H_{10}]$ is 10% and the initial precursor is $t$-BPO.

Figure 6. Joint probability density functions of the factorial variables corresponding to $A_{434}$ and $A_{444}$. Concentric circles are the PDFs of the prior model. Concentric ellipses are the PDFs of the posterior models considering measurements of absolute $[C_2H_4]$ and $[C_3H_6]$. The initial $[n-C_4H_{10}]$ varies from 10% (far left) to 0.01% (far right), and the initial precursor is $t$-BPO.

Figure 7. Joint probability density functions of the factorial variables corresponding to $A_{633}$ and $A_{108}$. Concentric circles are the PDFs of the prior model. Concentric ellipses are the PDFs of the posterior models considering measurements of absolute $[C_2H_4]$ and $[C_3H_6]$. The initial $[n-C_4H_{10}]$ varies from 10% (far left) to 0.01% (far right), and the initial precursor is $t$-BPO.

Figure 8. Joint probability density functions of the factorial variables corresponding to $A_{633}$ and $A_{634}$. Concentric circles are the PDFs of the prior model. Concentric ellipses are the PDFs of the posterior models considering measurements of absolute $[C_2H_4]$ and $[C_3H_6]$. The initial $[n-C_4H_{10}]$ varies from 10% (far left) to 0.01% (far right), and the initial precursor is $t$-BPO.
Figure 9. Joint probability density functions of the factorial variables corresponding to \( A_{633} \) and \( A_{634} \). Concentric circles are the PDFs of the prior model. Concentric ellipses are the PDFs of the posterior models considering measurements of \([C_2H_4]/[C_3H_6]\). The initial \([n-C_8H_{10}]\) varies from 10\% (far left) to 0.01\% (far right), and the initial precursor is HME; no toluene is used.

Figure 10. Joint probability density functions of the factorial variables corresponding to \( A_{633} \) and \( A_{634} \). Concentric circles are the PDFs of the prior model. Concentric ellipses are the PDFs of the posterior models considering measurements of \([C_2H_4]/[C_3H_6]\). The initial \([n-C_8H_{10}]\) varies from 10\% (far left) to 0.01\% (far right), and the initial precursor is HME; 2\% toluene is used as a radical inhibitor.