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Evaluated Rate Constants for *i*-Butane + H and CH₃: Shock Tube Experiments with Bayesian Model Optimization

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Abstract: The reactions of *i*-butane with CH₃ and H were investigated with shock tube experiments (870 K to 1130 K and 140 kPa to 360 kPa). Propene and *i*-butene, measured with GC/FID and MS, were quantified as characteristic of H-abstraction from the primary and tertiary carbons, respectively. A comprehensive Cantera[1] kinetics model based on JetSurF 2.0[2] was optimized to these experimental measurements and literature data – including early experiments at low temperatures, measurements of the total rate constant, and measurement from ethane for the rate constant for primary carbons – using the Method of Uncertainty Minimization using Polynomial Chaos Expansions (MUM-PCE) – pioneered by David Sheen and Hai Wang.[3] For both H and CH₃, the optimization increased the rate H-abstraction from the tertiary carbon relative to the primary carbon. We combined our primary and tertiary rate constants with previous results from our group on *n*-butane[4] to get site-specific rate constants for the reaction of H and CH₃ with a generic primary, secondary and tertiary carbon.

Key Words: *kinetics, pyrolysis, combustion, modeling, H-abstraction*

1. Introduction

Combustion chemistry is driven by chain reactions propagated by free radicals, like H and methyl (CH₃).[5] H and CH₃ radicals readily react with hydrocarbons, typically abstracting a H to form H₂ or CH₄, respectively. The rate of this reaction is highly dependent on the structure of the carbon center from which the H is abstracted. Due to the relative strengths of their C-H bonds, tertiary carbons react faster with H and CH₃ than secondary carbons, which react faster than primary carbons. The global structure and the mass of the alkane do not strongly affect the rate of hydrogen abstraction, so rate constants for a large hydrocarbon fuel are often calculated from the number of its primary, secondary and tertiary carbons.[6]

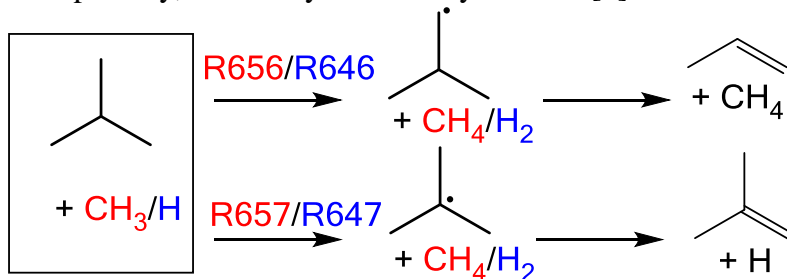


Figure 1. Reactions of CH₃ (red, reactions R656 and R657) and H (blue, reactions R646 and R647) with *i*-butane.

Here, we found relative rate constants for the reaction of *i*-butane with H and CH₃ radicals with shock tube experiments. The shock tube data was combined with literature data to find to

find rates for abstraction at both the primary and tertiary carbons using MUM-PCE. Combining primary and tertiary rate constants from this work with previous work on *n*-butane,[4] we propose self-consistent rate constants for H-abstraction from primary, secondary and tertiary carbon centers by H and CH₃.

2. Methods

All experiments were performed in the NIST shock tube reactor which has been described elsewhere.[4] H and CH₃ radicals were produced from pyrolysis of C₂H₅I and *di-tert*-butylperoxide (*dt*BPO), respectively. After the H or CH₃ reacted with an excess of *i*-butane, the products – especially propene and *i*-butene, produced from H-abstraction from the primary carbon and secondary carbons, respectively– were measured with gas chromatography with flame ionization and mass spectrometric detection. The ratio of [propene]/[*i*-butene] approximately equals the branching ratio of k_{656}/k_{657} for experiments with *dt*BPO and of k_{646}/k_{647} for experiments with C₂H₅I. An excess of toluene was added to scavenge free radicals. The shock temperature and pressure were (868 to 1131) K and (130 to 360) kPa.

Table 1. Rate Constants for the Main Reactions of the Prior Model. Parameters are for $k = A \times T^n \times \exp(-E_a/RT)$. A is in units of mol, s, cm. E_a/R is in units of K.

Reaction number	Reaction		log ₁₀ A	n	E _a /R	Reference
645	CH ₃ + <i>i</i> C ₃ H ₇ ↔ <i>i</i> C ₄ H ₁₀	k_∞	15.15	-0.68	0	JetSurF 2.0[2]
		k_0	61.62	-13.33	1964.3	
646	H + <i>i</i> C ₄ H ₁₀ ↔ H ₂ + <i>i</i> C ₄ H ₉	k	6.257	2.54	3400.	Tsang and JetSurF 2.0[2, 7]
647	H + <i>i</i> C ₄ H ₁₀ ↔ H ₂ + <i>t</i> C ₄ H ₉	k	5.780	2.4	1300.	
656	CH ₃ + <i>i</i> C ₄ H ₁₀ ↔ CH ₄ + <i>i</i> C ₄ H ₉	k	0.132	3.65	3600.	
657	CH ₃ + <i>i</i> C ₄ H ₁₀ ↔ CH ₄ + <i>t</i> C ₄ H ₉	k	-0.044	3.46	2314	
673	Toluene + H ↔ Benzyl + H ₂	k	14.17	0	4500.	Sheen <i>et al.</i> [8]
674	Toluene + H ↔ Benzene + CH ₃	k	6.230	2.2	2000.	Sheen <i>et al.</i> [8]
676	Toluene + CH ₃ ↔ Benzyl + CH ₄	k	11.50	0	4780.6	JetSurF 2.0[2, 9]
805	Benzyl + CH ₃ ↔ Ethylbenzene	k	13.08	0	111.2	Brand <i>et al.</i> [10]

We created a chemical model with the Cantera software package[1] based off the JetSurF 2.0 chemical mechanism.[2] This mechanism was modified by David Sheen to include compounds commonly used for shock tube experiments at NIST[11]:[4, 8] and C₂H₅I decomposition from Bentz *et al.* Rate constants for the decomposition of *i*-butyl radicals were taken from experiments in our laboratory that measured that *i*-C₄H₉ is dominated by C-C scission. Under 1050 K, the kinetics model predicts that >96 % of propene is from R646 and R656 – abstraction from the primary carbon. For the entire temperature range of the experiments, ≥97 % of *i*-butane is from abstraction from the tertiary carbon, R647 and R657.

The Cantera kinetics was optimized to the experimental data using Method of Uncertainty Minimization using Polynomial Chaos Expansions (MUM-PCE) with the mumpce 0.1 software package published by David Sheen.[3, 12] First we performed a sensitivity analysis to find what reactions – called “active parameters” – are most important to predicting the outcome of the shock experiment (Table 1). With Bayes theorem, MUM-PCE then optimized the active parameters’ rate constants to better match experimental data from the shock tube and relevant

literature data.[13] The literature data included measurements of raw experimental data, total rate constants ($k_p + k_s$), relative rate constants, and primary rate constants from ethane.

3. Results and Discussion

Product distributions are shown for a typical trial on Figure 2 for all species with abundances of 1 % or more of acetone. Besides acetone, which is produced from *dt*PBO decomposition, the two most abundant species are methane and ethane, both from CH_3 radical chemistry: methane from R656 and R657 and ethane from CH_3 self-recombination. As the main products of CH_3 reaction with *i*-butane, propene and *i*-butene were also detected in significant amounts. We also measured aromatic compounds from the reactions of CH_3 with toluene, including ethylbenzene (R805), benzene (R674, H reactant produced from R657) and bibenzyl. All products except acetone increase with temperature (Figure 2), and this increase accelerates above 1050 K. This correlates with the decomposition of *i*-butane (R645), which starts to decompose at 1050 K, producing additional CH_3 radicals.

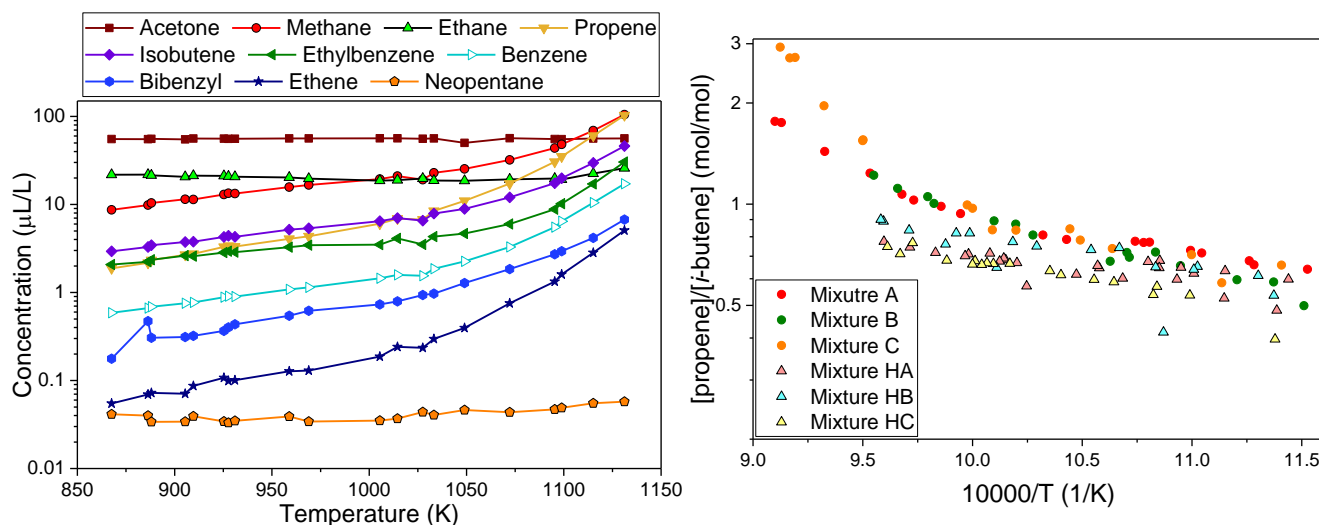


Figure 2. Left: Products a mixture with *dt*BPO. Right: $[\text{propene}]/[\textit{i}\text{-butene}]$ for all mixtures. Mixtures A, B and C have *dt*BPO and mixtures HA, HB and HC

As with mixtures *dt*BPO, mixtures with $\text{C}_2\text{H}_5\text{I}$ had significant amounts of *i*-butene and propene from R646 and R647, respectively. Since CH_3 radicals were produced as co-products with propene from R646, we observed methane at concentrations about equal to those of propene. Ethane concentration, due to the lower CH_3 concentrations for mixtures with $\text{C}_2\text{H}_5\text{I}$ – about an order of magnitude less than methane concentrations. We, again, measured significant amounts of benzene, ethylbenzene, and bibenzyl from toluene chemistry.

Assuming no side chemistry, the ratio of $[\text{propene}]/[\textit{i}\text{-butene}]$ is equal to the branching ratio of k_{646}/k_{647} for H-dominated mixtures with $\text{C}_2\text{H}_5\text{I}$ and k_{656}/k_{657} CH_3 -dominated mixtures with *dt*BPO. Figure 1 shows that for both H and CH_3 the ratio is about equal to 1 at temperatures between 868 and 1052K. This ratio increases with temperature, as tertiary abstraction is more favorable at lower temperatures due to the lower C-H bond strengths (and therefore lower activation energy for reaction R646 and R647) for tertiary carbons.[7] The branching ratio is higher for CH_3 than H, meaning that H is more selective for the tertiary carbon than CH_3 .

The data from these shock tube experiments (including measurements of the ratio, propene, ethene, benzene, methane and ethane). We used MUM-PCE to find the sensitivity of the prior model – or more specifically, the model’s predictions for all experiments used for the

optimization – to changing each of its 1487 rate constants. This analysis led to the choice of nine rate constants to optimize – which we call active parameters (Table 1). For most of these nine active parameters (Table 1), we only optimized the A-factor (which is the same as multiplying the rate constant by a temperature- and pressure-independent constant). For reactions R646, R647, R656, and R657, we optimized both the A-factor and the activation energy, E_a , as these reactions are the primary focus of this work and are the most well-constrained by our experiment and the chosen literature data.

Table 2. Posterior Active Parameters with Factorial Uncertainties (f_A for A and f_{E_a} for E_a). A is in units of mol, s, cm. E_a/R is in units of K.

Reaction number		$\log_{10}A$	f_A	n	E_a/R	f_{E_a}
645	k_∞	15.57	1.32	-0.68	0	-
	k_0	61.62	-	-13.33	1964.3	-
646	k	6.17	1.55	2.54	3390	1.09
647	k	5.88	1.45	2.4	1409	1.18
656	k	0.233	1.67	3.65	3819	1.14
657	k	0.191	1.41	3.46	2362	1.08
673	k	14.23	1.42	0	4500	-
674	k	6.15	1.35	2.2	2000	-
676	k	11.54	1.45	0	4780.6	-
805	k	12.83	1.61	0	111.2	-

We first optimized all active parameters on Table 1 to only our data. We updated the kinetics model with the optimized rate constants for R645, R673, R673, R676 and R805, and reoptimized R646, R647, R656 and R657 to (1) the literature data and (2) our rate constants for R646, R647, R656 and R657 found from the first optimization. This two-step optimization was done so that our data would have approximately equal weight to the other experiments.

The posterior model also well describes our experimental data for most products and most experimental conditions, to within 35 %. The optimization decreased this relative rate constant to match the experimental ratios. From 950 -1200 K the ratio of k_{656}/k_{657} was lowered by (61 to 62) %, mostly due to a 72 % increase in the A-factor for CH₃ reaction with the tertiary carbon of *i*-butane (R657). The optimization also increased the relative amount of tertiary abstraction for H reaction with *i*-butane (26 to 28) % from 950 K to 1100 K, by increasing the A-factor of R647 by 25 % and decreasing the A-factor of R646 by 18 %.

The relative rate constants for the posterior model are (again, on a per-H basis):

$$\text{H} + i\text{-butane: } k_p/k_t = 10^{(-0.660 \pm 0.250)} \times T^{0.14} \times \exp(-(1982 \pm 397)/T)$$

$$\text{CH}_3 + i\text{-butane: } k_p/k_t = 10^{(-0.912 \pm 0.268)} \times T^{0.19} \times \exp(-(1457 \pm 567)/T)$$

and are applicable to temperatures from (270 to 1327) K. All uncertainties are 2σ .

By combining k_p and k_t from this work with k_s/k_p (k_s denotes the rate constant for H-abstraction from a secondary carbon) from previous work by Manion *et al.*[4] on *n*-butane, we provide a full set of self-consistent rate constants for H and CH₃ H-abstraction from primary, secondary and tertiary carbons. For both CH₃ and H reaction with a generic hydrocarbon, we use H-abstraction rate constants for primary carbons from this work, and find the secondary rate constant by multiplying the relative rate constants by Manion *et al.*[4] for k_s/k_p by our value of k_p . While Manion *et al.* did find rate constants for k_p with MUM-PCE for both H and CH₃, the values of k_p from this work are based on a larger data set.

Reaction Kinetics

We found the following rate constants for H reaction with a generic hydrocarbon on a per-H basis, (270 to 1327) K:

$$\begin{aligned} k_p &= 10^{(5.22 \pm 0.19)} \times n^{2.54} \times \exp(-3391 \pm 305) \text{ K} / T \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \\ k_s &= 10^{(5.64 \pm 0.20)} \times n^{2.4} \times \exp(-2145 \pm 336) \text{ K} / T \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \\ k_t &= 10^{(5.88 \pm 0.16)} \times n^{2.4} \times \exp(-1409 \pm 253) \text{ K} / T \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \end{aligned}$$

These values are plotted on Figure 3 and compared to evaluated rate constants by Tsang.[7, 14] The rate constants are only slightly updated from the prior model.

We found the following rate constants for CH₃ reaction with a generic hydrocarbon on a per-H basis, (270 to 1327) K:

$$\begin{aligned} k_p &= 10^{(-0.722 \pm 0.223)} \times n^{3.65} \times \exp(-3819 \pm 535) \text{ K} / T \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \\ k_s &= 10^{(0.095 \pm 0.231)} \times n^{3.46} \times \exp(-3193 \pm 547) \text{ K} / T \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \\ k_t &= 10^{(0.191 \pm 0.149)} \times n^{3.46} \times \exp(-2362 \pm 189) \text{ K} / T \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \end{aligned}$$

These values are plotted and compared to evaluated rate constants from Tsang.[7, 15] While the primary rate constant agrees well with Tsang, our rate constants for abstraction from a secondary carbon and tertiary carbons are slightly lower and slightly higher, respectively, than Tsang's rate constants.

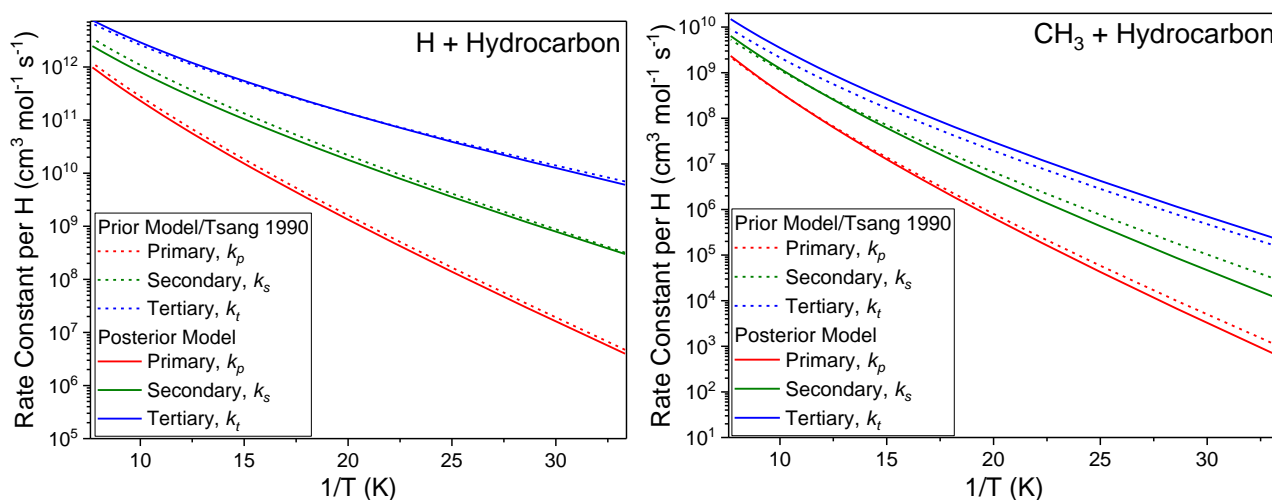


Figure 3. Our evaluated rate constants for H and CH₃ + a generic primary, secondary and tertiary carbon on a per-H basis compared to previous values by Tsang.[7, 15]

As expected due to the relative bond strengths, the activation energy for H-abstraction decreases from primary to secondary to tertiary for reaction with both H and CH₃. The A-factors increase from primary to secondary to tertiary, which ensures that the rate constants will not cross if they are extrapolated to higher temperatures. The rate constant for H and CH₃ reaction with any hydrocarbon can be found with the following formulate:

$$k_{total} = k_p \times N_{Hp} + k_s \times N_{Hs} + k_t \times N_{Ht}$$

where N_{Hp} , N_{Hs} , and N_{Ht} are the number of H's attached to primary, secondary and tertiary carbons, respectively.

4. Conclusions

We successfully used the MUM-PCE software package[12] to provide evaluated rate constants for H and CH₃ reaction with *i*-butane. The MUM-PCE method optimized a Cantera kinetics model to the experimental data we found using the NIST shock tube as well as to a range of literature data. The resulting rate constants were combined with previous work from our

laboratory on *n*-butane[4] to give self-consistent rate constants for H and CH₃ abstraction of a generic H on primary, secondary and tertiary carbons.

9. Acknowledgments

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10. References

- [1] D.G. Goodwin, H.K. Moffat, and R.L. Speth, *Cantera*. 2017.
- [2] Wang, H., et al., *JetSurF version 2.0*. 2010.
- [3] D.A. Sheen and H. Wang, The method of uncertainty quantification and minimization using polynomial chaos expansions, *Combust. Flame* 158 (2011) 2358-2374.
- [4] J.A. Manion, D.A. Sheen, and I.A. Awan, Evaluated Kinetics of the Reactions of H and CH₃ with *n*-Alkanes: Experiments with *n*-Butane and a Combustion Model Reaction Network Analysis, *J. Phys. Chem. A* 119 (2015) 7637-7658.
- [5] H.J. Curran, Rate constant estimation for C-1 to C-4 alkyl and alkoxy radical decomposition, *International Journal of Chemical Kinetics* 38 (2006) 250-275.
- [6] N. Cohen, Are reaction rate coefficients additive? Revised transition state theory calculations for OH + alkane reactions, *International Journal of Chemical Kinetics* 23 (1991) 397-417.
- [7] W. Tsang, Chemical Kinetic Data Base for Combustion Chemistry Part 4. Isobutane, *Journal of Physical and Chemical Reference Data* 19 (1990) 1-68.
- [8] D.A. Sheen, C.M. Rosado-Reyes, and W. Tsang, Kinetics of H atom attack on unsaturated hydrocarbons using spectral uncertainty propagation and minimization techniques. *Proceedings of the Combustion Institute*, 34 (2013) 527-536.
- [9] J. A. Kerr and M. J. Parsonage, Evaluated Kinetic Data on Gas Phase Hydrogen Transfer Reactions of Methyl Radicals, *Berichte der Bunsengesellschaft für physikalische Chemie*, 80 (1976) 825-825.
- [10] U. Brand, *et al.*, Carbon-carbon and carbon-hydrogen bond splits of laser-excited aromatic molecules. 1. Specific and thermally averaged rate constants, *J. Phys. Chem.* 94 (1990) 6305-6316.
- [11] D.A. Sheen. Personal correspondence.
- [12] D.A. Sheen. mumpce 0.1 documentation, 2017 April 6, Available from: https://davidasheen.github.io/mumpce_py/#
- [13] J. A. Manion, *et al.*, NIST Chemical Kinetics Database, NIST Standard Reference Database 17, Version 7.0 (Web Version), Release 1.6.8, Data version 2015.12, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899-8320. <http://kinetics.nist.gov/>
- [14] W. Tsang, Chemical kinetic data-base for combustion chemistry. 3. Propane. *Journal of Physical and Chemical Reference Data*, 17 (1988) 887-952.
- [15] W. Tsang, Chemical Kinetic Data Base for Combustion Chemistry 5. Propene. *Journal of Physical and Chemical Reference Data*, 20 (1991) 221-273