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Ehson Fawad Nasir, and Aamir Farooq

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**A Shock Tube Study of the CO + OH Reaction Near the Low-
Pressure Limit**

Ehson F. Nasir¹, Aamir Farooq*¹

¹ King Abdullah University of Science and Technology (KAUST), Clean Combustion Research
Center (CCRC), Physical Science and Engineering Division (PSE), Thuwal 23955-6900, Saudi
Arabia

*Corresponding Author:

Email: aamir.farooq@kaust.edu.sa

Phone: +966-128082704

Abstract

Rate coefficients for the reaction between carbon monoxide and hydroxyl radical were measured behind reflected shock waves over 700 – 1230 K and 1.2 – 9.8 bar. The temperature/pressure conditions correspond to the predicted low-pressure limit of this reaction, where the channel leading to carbon dioxide formation is dominant. The reaction rate coefficients were inferred by measuring the formation of carbon dioxide using quantum cascade laser absorption near 4.2 μm . Experiments were performed under pseudo-first order conditions with tert-butyl hydroperoxide (TBHP) as the OH precursor. Using ultraviolet laser absorption by OH radicals, the TBHP decomposition rate was measured to quantify potential facility effects under extremely dilute conditions used here. The measured CO + OH rate coefficients are provided in Arrhenius form for three different pressure ranges:

$$k_{\text{CO}+\text{OH}}(1.2 - 1.6 \text{ bar}) = (9.14 \pm 2.17) \times 10^{-13} \exp(-(1265 \pm 190)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{\text{CO}+\text{OH}}(4.3 - 5.1 \text{ bar}) = (8.70 \pm 0.84) \times 10^{-13} \exp(-(1156 \pm 83)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{\text{CO}+\text{OH}}(9.6 - 9.8 \text{ bar}) = (7.48 \pm 1.92) \times 10^{-13} \exp(-(929 \pm 192)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The measured rate coefficients are found to be lower than the master equation modeling results by Weston et al. [J. Phys. Chem. A, 117 (2013) 821] at 819 K and in closer agreement with the expression provided by Joshi and Wang [Int. J. Chem. Kinet., 38 (2006) 57].

1. Introduction

The reaction between carbon monoxide and the hydroxyl radical is considered the principal pathway for heat release and carbon dioxide formation in most hydrocarbon combustion systems.

Previous studies have shown that the laminar flame speed has the second highest sensitivity to the CO + OH reaction (after the H + O₂ chain-branching reaction), particularly for large alkanes¹⁻² and oxygenates³. As a result of its significance, the reaction has been the focus of many experimental and modeling efforts. The relevant references for these works can be found in recent publications by Joshi and Wang⁴ and by Weston et al.⁵ The CO + OH reaction has two product pathways:

The branching ratio between these pathways is heavily in favor of k_{1a} in the low-pressure limit of the reaction, whereas at high pressure, the k_{1b} channel gains significance due to the stabilization of the activated complex HOCO. For most combustion applications, the rate remains within the low-pressure limit as given, for example, by the expression in Joshi and Wang⁴.

Measurements of this rate have been carried out in various experimental arrangements. Brabbs et al.⁶ performed an indirect rate determination for the temperature range 1300-1900 K using a shock tube with H₂-O₂-CO mixtures. Similar mixtures were used by Vandooren et al.⁷ in a lean flame where the rate was determined using a molecular beam mass spectrometer. These rate determinations were indirect in nature as the experimental conditions were not uniquely

sensitive to the target rate and, therefore, required additional assumptions to deduce the rate constant with the help of a kinetic model. More direct determinations of this rate at high temperature were performed by Wooldridge and Hanson⁸ using HNO_3 as the OH precursor. Lower temperature (< 1100 K) studies were carried out in flow reactor experiments using excitation techniques such as flash photolysis⁹⁻¹¹ or electron beam excitation¹² to generate OH from the appropriate gas mixtures. It should be noted that, with the exception of Fulle et al.¹⁰, all previous low-temperature determinations were well within the low-pressure limit of k_1 . In low-temperature combustion environments, such as HCCI engines, the operating conditions are typically not very far from the low-pressure limit and, therefore, it is important to study the CO + OH reaction in the vicinity of the low-pressure limit.

In this work, rate coefficients for k_{1a} were measured near the low-pressure limit in pseudo-first order shock tube experiments. Hydroxyl radicals were generated by thermal decomposition of tert-butyl hydroperoxide (TBHP) which is known to be a clean OH precursor¹³. A sensitive infrared laser absorption sensor was used to measure CO_2 concentration profiles which were found to be mainly sensitive to k_{1a} and the TBHP decomposition rate, also measured as part of this study. The use of highly sensitive laser absorption technique allowed for a more accurate determination of the rate coefficient compared to previous low-temperature studies. This work represents, to our knowledge, the first measurement of k_{1a} at low temperatures in a shock tube facility.

2. Experimental Method

2.1 Shock Tube Facility

All experiments were carried out behind reflected shock waves in the low-pressure shock tube facility at King Abdullah University of Science and Technology (KAUST). The facility has been described previously¹⁴ and only a brief overview will be provided here. The shock tube is electro-polished with an inner diameter of 14.2 cm and a driven section length of 9 m. The length of the driver section can be increased up to 9 m depending on the required test times. The test times in this work were 1-2 milliseconds and the uncertainties in reflected shock conditions (T , P) were less than 1%. The laser diagnostics (CO_2 and OH) used in this study were aligned at an axial plane 2 cm from the shock tube endwall, as shown in Fig. 1. High-purity (99.999%) argon and carbon monoxide were used for preparing reactant mixtures. A 70% TBHP solution in water was supplied by Sigma-Aldrich. Gaseous mixtures were prepared manometrically in a 24-litre magnetically-stirred mixing vessel. The shock tube was turbo-pumped between experiments down to 5×10^{-5} mbar to maintain high purity of the reactive environment.

Fig. 1. Experimental schematic showing the planar cross-section of the shock tube 2 cm from the endwall.

2.2 Hydroxyl Precursor and Laser Diagnostic

Several previous investigations of rate measurements for reactions involving OH have employed TBHP as a fast, clean source of OH over a wide temperature range (800 – 1300 K)¹⁵⁻¹⁷. Hydroxyl radicals are generated via the following decomposition reaction:

For temperatures greater than 1000 K, TBHP decomposition is near instantaneous after the arrival of the reflected shock wave. This allows the initial TBHP concentration to be determined from the peak OH yield via an *in-situ* OH diagnostic. This determination is necessary due to the adsorption of TBHP to the mixing vessel and shock tube walls which results in a lower TBHP concentration than that determined manometrically. For temperatures lower than 1000 K, the time scale of TBHP decomposition is longer and therefore the peak OH yield no longer provides a measure of the initial TBHP concentration. In this study, high- and low- temperature measurements were alternated so that the initial TBHP concentration determined from the high-temperature cases can be used in the low-temperature cases. The TBHP concentration measured using this method did not vary by more than 10% between consecutive high-temperature cases. Based on the measured TBHP concentration, the water vapor mole fraction was estimated through Rault's law. Previously, Pang et al.¹³ had shown that water vapor does not have any significant effect on TBHP kinetics under highly dilute conditions.

A ring-dye laser system with external frequency doubling, details of which can be found in the work by Badra et al.¹⁸, was used to generate laser light near 306 nm to measure OH mole fraction using the Beer-Lambert relation, $I/I_0 = \exp(-k_{\text{OH}}X_{\text{OH}}PL)$. Here, I_0 and I refer to incident and transmitted laser intensities respectively, k_{OH} is the absorption coefficient, X_{OH} is the OH mole fraction, P is the pressure and L is the absorption path length (inner diameter of shock

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3 tube). For the conditions of interest, this diagnostic provides a noise-limiting detection limit of
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5 0.1 ppm.
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10 **2.2 CO₂ Laser Diagnostic**

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13 An external cavity quantum cascade laser (Daylight Solutions) operating near 4.2 μm was
14 used to measure CO₂ concentration *via* the R(32) ro-vibrational transition in the ν_3 band of CO₂.
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16 Absorption cross-sections at the peak of this line were measured in separate experiments of
17 shock-heated CO₂-Ar mixtures over 700 – 2000 K and 1 – 10 bar. These measurements are
18 provided in the Supplementary Material. As with the OH diagnostic, the CO₂ concentrations
19 were calculated using the Beer-Lambert law. Compared with previous diagnostics based on the
20 ν_3 band¹⁹, this sensor provides much higher sensitivity for these conditions with a noise-limiting
21 detection limit of 2 ppm. Since CO₂ in the ambient air also strongly absorbs the laser intensity at
22 this wavelength, a nitrogen purging setup was used over the entire laser path from the laser
23 source to the photo-detector, as shown in Fig. 1.
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37 **3. Results and Discussion**

38 **3.1 Sensitivity Analyses**

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41 The experimental results were modeled using the modified JetSurF 1.0 mechanism,
42 which contains TBHP reactions provided by Pang et al.¹³. Sensitivity analyses and kinetic
43 simulations were performed using the ChemKin-Pro software package. Figures 2 and 3 show the
44 reactions contributing significantly to the sensitivity coefficient of OH and CO₂, respectively.
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46 From these analyses, it is evident that the CO₂ concentration profile is more sensitive to the
47 target rate k_{1a} as compared to the OH profile for which other reactions are more significant
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contributors. Therefore, in this work, k_{1a} was determined by fitting the kinetic simulation results to the measured CO_2 profiles.

Fig. 2. Hydroxyl sensitivity analysis using the modified JetSurF mechanism²⁰. Simulation conditions: $T = 862 \text{ K}$, $P = 1.52 \text{ bar}$, 120 ppm TBHP / 180 ppm H_2O / 0.5% CO / Ar (bath gas).

Fig. 3. Carbon dioxide sensitivity analysis using the mechanism and conditions of Fig. 2.

3.2 TBHP Kinetics

Figure 2 illustrated the significant contribution of k_2 (TBHP decomposition) on the CO_2 sensitivity, indicating that the uncertainty in this rate will affect determination of k_{1a} . Direct measurements of k_2 using TBHP/Ar mixtures have only been performed previously by Pang et al.¹³ We decided to make a similar rate determination for k_2 to compare against results by Pang et al. and to investigate the suitability of our shock tube facility for experiments in highly dilute conditions. Figure 4 shows a representative experimental OH trace from a TBHP decomposition experiment. The modified JetSurF mechanism was used to fit the measured OH traces over 755 – 989 K and 1.2 – 1.6 bar to obtain the following Arrhenius expression for k_2 :

$$k_2 = 8.43 \times 10^{13} \exp(-18649/T) \text{ s}^{-1} \quad (3)$$

Fig. 4. Measured OH mole fraction trace for TBHP decomposition. Overlaid are simulation results using the JetSurF mechanism along with perturbations of $\pm 20\%$. Conditions: $T = 755 \text{ K}$, $P = 1.52 \text{ bar}$, $33.5 \text{ ppm TBHP} / 50.3 \text{ ppm H}_2\text{O} / \text{Ar}$ (bath gas).

Figure 5 shows a comparison between this rate expression and that of Pang et al.¹³ where a similar experimental methodology was employed. Our measured activation energy is slightly higher than that of Pang et al.¹³ resulting in about a 30% higher value of the rate constant close to

1000 K. The deviation between the two rate expressions decreases at lower temperatures with almost identical values near 700 K. Our measured results are therefore consistent with the reported uncertainty of $\pm 30\%$ by Pang et al.¹³. Moreover, it should be noted that the effect of k_2 on the CO_2 sensitivity in CO/TBHP/Ar experiments decreases with increasing temperature, and, therefore, the deviation in k_2 close to 1000 K is not expected to have a large effect on the determination of k_{1a} .

Fig. 5. Comparison of the TBHP decomposition rate between this work and Pang et al.¹³

3.3 CO + OH Rate Measurements

The CO + OH rate was measured under pseudo-first order reaction conditions where the TBHP concentration was nominally kept between 100 – 150 ppm and CO in excess at 0.5%. This led to the CO_2 concentration profile being sensitive to k_{1a} , as exemplified by Fig. 3. Measurements were conducted over conditions (700 – 1230 K and 1.2 – 9.8 bar) not covered by previous shock tube studies. Figure 6 shows a representative CO_2 trace at 1.43 atm for a mixture of 116 ppm TBHP / 174 ppm H_2O / 0.5% CO / Ar. The $\pm 20\%$ perturbations illustrate the

sensitivity of the measured CO₂ profiles to the target reaction rate. The measured rate constants are plotted in Fig. 7 in Arrhenius form for the three pressure ranges investigated here. Due to the relatively narrow temperature range investigated in this study, the results for each pressure range can be fitted to a simple Arrhenius expression. The respective Arrhenius expressions for the three pressure ranges are given as follows (including fitting errors):

$$k_{1a}(1.2 - 1.6 \text{ bar}) = (9.14 \pm 2.17) \times 10^{-13} \exp(-(1265 \pm 190)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{1a}(4.3 - 5.1 \text{ bar}) = (8.70 \pm 0.84) \times 10^{-13} \exp(-(1156 \pm 83)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{1a}(9.6 - 9.8 \text{ bar}) = (7.48 \pm 1.92) \times 10^{-13} \exp(-(929 \pm 192)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Fig. 6. Measured CO₂ mole fraction trace overlaid with simulation results using the JetSurF mechanism along with perturbations of $\pm 20\%$. Conditions: $T = 962 \text{ K}$, $P = 1.45 \text{ bar}$, $116 \text{ ppm TBHP} / 174 \text{ ppm H}_2\text{O} / 0.5\% \text{ CO} / \text{Ar}$ (bath gas).

Fig. 7. Measured rate constants and Arrhenius fits for k_{1a} .

The expression for the low-pressure limit given by Joshi and Wang⁴ suggests that the pressure range used in the current study is near the low-pressure limit. However, as illustrated by Fig. 7, the measured rate constant is slightly pressure dependent. This is even more prominent in Fig. 8 where interpolated rate constant values at 819 K are plotted against the total number density. The pressure dependence of k_1 has been evaluated in recent works via master equation modeling by Joshi and Wang⁴ and by Weston et al.⁵ at selected temperatures for comparison with experimental results of Fulle et al.¹⁰ Figure 8 shows such a comparison at 819 K wherein experimental data points other than those by Fulle et al.¹⁰ are interpolated results. The calculated low-pressure limit rate constant differs by approximately 22% between the modeling results of Wang and Weston et al.^{4,5} The data points from the current work are found to be lower than both of these calculations albeit being closer to Joshi and Wang⁴.

Fig. 8. Pressure dependence of k_1 at 819 K including results from experiments¹⁰⁻¹² and master equation modeling⁴⁻⁵.

Based on the expression for the low-pressure limit given by Joshi and Wang (Eq. 22 in Ref 4) and the results from Fig. 8, the measured rate constants for the pressure range 1.2 – 1.6 bar can be assumed to be at the low-pressure limit for comparison purposes. Figure 9 shows the measured low-pressure data from this work compared with flow reactor results by Westenberg et al.⁹ and Ravishankara et al.¹¹ and shock tube measurements by Wooldridge and Hanson⁸. Also shown are the theoretical results by Joshi and Wang⁴. The fit to the current work is found to be lower than most of the literature measurements and systematically lower than the calculation by Joshi and Wang by 30% or more. This difference can be attributed to two main factors: the choice of the OH precursor and the sensitivity of the detection technique. The OH precursor used in this work (TBHP) has well-characterized secondary chemistry and can be used in highly dilute conditions, as opposed to previous works involving less efficient OH production methods. The detection technique for CO₂ employed in this study has been shown to be relatively free from interference from secondary effects and is highly quantitative as opposed to the relatively broadband techniques used for OH in previous works.

Fig. 9. Arrhenius plot for k_1 at the low-pressure limit from literature^{4, 8-9, 11} and the current data for the pressure range 1.2-1.6 bar.

4. Uncertainty in Rate Measurements

Major sources of uncertainty in k_{1a} are given in Table 1 for a representative low temperature case. Other cases at the extremes of the conditions used in this work can be found in the Supplementary Material. The individual uncertainty contributions to the final rate were determined by applying the listed perturbations and re-fitting the rate constant through kinetic simulations. The most significant contribution to the overall uncertainty is from the TBHP decomposition rate k_2 because the sensitivity to k_2 is more significant at lower temperatures. As stated previously, the uncertainty in k_2 is taken to be the same as that by Pang et al.¹³, i.e., $\pm 30\%$.

Uncertainties associated with the CO_2 diagnostic arise from uncertainty in the absorption coefficient and noise in the detection system. The uncertainty in initial TBHP concentration is taken to be the maximum variation in measured peak OH mole fractions for high-temperature cases, i.e., $\pm 10\%$. The H_2O concentration in the reactive system did not have a significant effect on the uncertainty, as found by Pang et al.¹³ for similar conditions. While the uncertainty in the

reflected shock temperature is found to have an effect on the overall uncertainty, the uncertainty in reflected shock pressure has negligible influence on the measured rate constant. Moreover, the effect of vibrational relaxation of CO is also negligible due to equilibrium population of CO being overwhelmingly in the ground state at these temperatures, as was noted by Wooldridge and Hanson⁸.

Table 1. Major sources of uncertainty in k_{1a} for $T=862\text{ K}$, $P=1.52\text{ bar}$, 120 ppm TBHP / 180 ppm H_2O / 0.5 % CO / Ar (bath gas).

Parameter	Uncertainty	Effect on k_{1a}
TBHP Decomposition Rate, k_2	30%	14.6%
CO ₂ Diagnostic	5%	6.92%
Initial TBHP concentration	10%	4.62%
Reflected Shock Temperature, T	1%	3.85%
Total		17.3%

5. Conclusions

Rate constants for the CO + OH reaction have been measured near the low-pressure limit for temperature of interest to low-temperature combustion. Compared to previous theoretical determinations, the measured rate constants have been found to be systematically lower for these conditions. The calculated low-pressure limit rate constant by Joshi and Wang⁴ is found to be closest to our measurements. The low detection limit of the CO₂ diagnostic used in this work allows for a more accurate determination of the rate constant at these conditions leading to lower uncertainties in the modeling of low-temperature combustion phenomena.

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References

1. Kumar, K.; Sung, C.-J., Laminar flame speeds and extinction limits of preheated n-decane/o₂/n₂ and n-dodecane/o₂/n₂ mixtures. *Combust. Flame* **2007**, *151* (1–2), 209-224.
2. Ji, C.; Dames, E.; Wang, Y. L.; Wang, H.; Egolfopoulos, F. N., Propagation and extinction of premixed c₅–c₁₂ n-alkane flames. *Combust. Flame* **2010**, *157* (2), 277-287.
3. Cai, L.; Sudholt, A.; Lee, D. J.; Egolfopoulos, F. N.; Pitsch, H.; Westbrook, C. K.; Sarathy, S. M., Chemical kinetic study of a novel lignocellulosic biofuel: Di-n-butyl ether oxidation in a laminar flow reactor and flames. *Combust. Flame* **2014**, *161* (3), 798-809.
4. Joshi, A. V.; Wang, H., Master equation modeling of wide range temperature and pressure dependence of $\text{co} + \text{oh} \rightarrow \text{products}$. *Int. J. Chem. Kinet.* **2006**, *38* (1), 57-73.
5. Weston, R. E.; Nguyen, T. L.; Stanton, J. F.; Barker, J. R., $\text{Ho} + \text{co}$ reaction rates and h/d kinetic isotope effects: Master equation models with ab initio scst rate constants. *J. Phys. Chem. A* **2013**, *117* (5), 821-835.
6. Brabbs, T. A.; Belles, F. E.; Brokaw, R. S., Shock-tube measurements of specific reaction rates in the branched-chain $\text{h}_2\text{-co-o}_2$ system. *Proc. Combust. Inst.* **1971**, *13* (1), 129-136.
7. Vandooren, J.; Peeters, J.; Tiggelen, P. J. V., Rate constant of the elementary reaction of carbon monoxide with hydroxyl radical. *Proc. Combust. Inst.* **1975**, *15* (1), 745-753.
8. Wooldridge, M. S.; Hanson, R. K.; Bowman, C. T., A shock tube study of the $\text{co+oh} \rightarrow \text{co}_2 + \text{h}$ reaction. *Proc. Combust. Inst.* **1994**, *25* (1), 741-748.

9. Westenberg, A. A.; deHaas, N., Rates of $\text{CO} + \text{OH}$ and $\text{H}_2 + \text{OH}$ over an extended temperature range. *J. Chem. Phys.* **1973**, *58* (10), 4061-4065.
10. Fulle, D.; Hamann, H. F.; Hippler, H.; Troe, J., High pressure range of addition reactions of HO. II. Temperature and pressure dependence of the reaction $\text{HO} + \text{CO} \rightleftharpoons \text{HOCO} \rightarrow \text{H} + \text{CO}_2$. *J. Chem. Phys.* **1996**, *105* (3), 983-1000.
11. Ravishankara, A. R.; Thompson, R. L., Kinetic study of the reaction of OH with CO from 250 to 1040 K. *Chem. Phys. Lett.* **1983**, *99* (5-6), 377-381.
12. Beno, M. F.; Jonah, C. D.; Mulac, W. A., Rate constants for the reaction $\text{OH} + \text{CO}$ as functions of temperature and water concentration. *Int. J. Chem. Kinet.* **1985**, *17* (10), 1091-1101.
13. Pang, G. A.; Hanson, R. K.; Golden, D. M.; Bowman, C. T., High-temperature measurements of the rate constants for reactions of OH with a series of large normal alkanes: N-pentane, n-heptane, and n-nonane. *Z. Phys. Chem.* **2011**, *225* (11-12), 1157.
14. Javed, T.; Nasir, E. F.; Es-sebbar, E.-t.; Farooq, A., A comparative study of the oxidation characteristics of two gasoline fuels and an n-heptane/iso-octane surrogate mixture. *Fuel* **2015**, *140* (0), 201-208.
15. Bott, J. F.; Cohen, N., A shock tube study of the reaction of the hydroxyl radical with propane. *Int. J. Chem. Kinet.* **1984**, *16* (12), 1557-1566.
16. Vasudevan, V.; Davidson, D. F.; Hanson, R. K., Direct measurements of the reaction $\text{OH} + \text{CH}_2\text{O} \rightarrow \text{HCO} + \text{H}_2\text{O}$ at high temperatures. *Int. J. Chem. Kinet.* **2005**, *37* (2), 98-109.
17. Badra, J.; Nasir, E. F.; Farooq, A., Site-specific rate constant measurements for primary and secondary H- and D-abstraction by OH radicals: Propane and n-butane. *J. Phys. Chem. A* **2014**, *118* (26), 4652-4660.

18. Badra, J.; Elwardany, A. E.; Khaled, F.; Vasu, S. S.; Farooq, A., A shock tube and laser absorption study of ignition delay times and oh reaction rates of ketones: 2-butanone and 3-buten-2-one. *Combust. Flame* **2014**, *161* (3), 725-734.
19. Spearrin, R. M.; Ren, W.; Jeffries, J. B.; Hanson, R. K., Multi-band infrared co2 absorption sensor for sensitive temperature and species measurements in high-temperature gases. *Appl. Phys. B* **2014**, *116* (4), 855-865.
20. B. Sirjean; E. Dames, D. A. S., X.-Q. You, C. Sung, A. T. Holley, F. N. Egolfopoulos, H. Wang, S. S. Vasu, D. F. Davidson, R. K. Hanson, C. T. Bowman, A. Kelley, C. K. Law, W. Tsang, N. P. Cernansky, D. L. Miller, A. Violi, R. P. Lindstedt, A high-temperature chemical kinetic model of n-alkane oxidation. In *JetSurF version 1.0*.

TOC Graphic: