Site-Specific Reaction Rate Constant Measurements for Various Secondary and Tertiary H-Abstraction by OH

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Abstract

Reaction rate constants for nine site-specific hydrogen atom (H) abstraction by hydroxyl radicals (OH) have been determined using experimental measurements of the rate constants of Alkane + OH $\rightarrow$ Products reactions. Seven secondary (S_{20} , S_{21} , S_{22} , S_{30} , S_{31} , S_{32} , and S_{33}) and two tertiary (T_{100} and T_{101}) site-specific rate constants, where the subscripts refer to the number of carbon atoms (C) connected to the next-nearest-neighbor (N-N-N) C atom, were obtained for a wide temperature range (250 – 1450 K). This was done by measuring the reaction rate constants for H abstraction by OH from a series of carefully selected large branched alkanes. The rate constant of OH with four different alkanes, namely 2,2-dimethyl-pentane, 2,4-dimethyl-pentane, 2,2,4-trimethyl-pentane (iso-octane), and 2,2,4,4-tetramethyl-pentane were measured at high temperatures (822 to 1367 K) using a shock tube and OH absorption diagnostic. Hydroxyl radicals were detected using the narrow-line-width ring-dye laser absorption of the $R_1(5)$ transition of OH spectrum near 306.69 nm.

Previous low-temperature rate constant measurements are added to the current data to generate three-parameter rate expressions that successfully represent the available direct measurements over a wide temperature range (250 – 1450 K). Similarly, literature values of the low-temperature rate constants for the reaction of OH with seven normal and branched alkanes are combined with the recently measured high-temperature rate constants from our group [1]. Subsequent to that, site-specific rate constants for abstractions from various types of secondary and tertiary H atoms by OH radicals are derived and have the following modified Arrhenius expressions:

$$S_{20} = 8.49 \times 10^{-17} T^{1.52} \exp(73.4 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (250 – 1450 K)}$$

$$S_{21} = 1.07 \times 10^{-15} T^{1.07} \exp(208.3 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (296 – 1440 K)}$$

$$S_{22} = 2.88 \times 10^{-13} T^{0.41} \exp(-291.5 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (272 – 1311 K)}$$

$$S_{30} = 3.35 \times 10^{-18} T^{1.97} \exp(323.1 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (250 - 1366 \text{ K})$$

$$S_{31} = 1.60 \times 10^{-18} T^{2.0} \exp(500.0 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (250 - 1351 \text{ K})$$

$$S_{32} = 9.65 \times 10^{-17} T^{1.45} \exp(180.0 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (297 - 1367 \text{ K})$$

$$S_{33} = 2.83 \times 10^{-19} T^{2.25} \exp(501.3 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (250 - 1365 \text{ K})$$

$$T_{100} = 5.69 \times 10^{-16} T^{1.32} \exp(76.8 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (297 - 1375 \text{ K})$$

$$T_{101} = 1.05 \times 10^{-16} T^{1.38} \exp(577.9 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (297 - 1362 \text{ K})$$

Keywords: alkanes; hydroxyl radicals; rate constants; shock tube; site-specific rates.

1. Introduction

Gasoline, diesel, and aviation fuels [2-4] are mainly composed of straight and branched large alkanes. Volatile organic compounds (VOCs) contain significant amount of alkanes [5] which react with hydroxyl (OH) radicals in the atmosphere. Hydroxyl are important reactive radicals in combustion and atmospheric chemistry, and it is widely accepted that OH radicals oxidation of hydrocarbon fuels is the major oxidation route for these molecules under atmospheric and combustion conditions [6-8]. Despite the significant importance of this reaction in atmospheric and combustion temperatures, there is a lack of direct rate constant measurements for OH with large alkanes, particularly at high temperatures.

Review articles by Atkinson [9-13] summarized the gas-phase reaction rate constants of OH radicals with various alkanes for a wide temperature range (250 – 1200 K). Tully and co-workers [14-19] studied the reaction rate of OH with various alkanes (normal, cyclic, and branched alkanes ranging from C₁ to C₈) to determine the site-specific (primary, secondary, and tertiary) rate constants of H- and D-abstraction by the OH radicals at temperatures below 900 K. Their work was complemented by single-point high-temperature (1100 – 1200 K) measurements performed by Cohen and co-workers [20-24]. Because of the significant curvature exhibited by these rate constants, as shown in refs [14-24], more direct measurements at higher temperatures were needed. Sivaramakrishnan et al. [25, 26] measured the reaction rate constants of OH with a few normal and branched alkanes at high temperatures (797 K – 1259 K). Pang et al. [27] measured the rate constants of n-pentane, n-heptane and n-nonane with OH at temperatures ranging from 869 to 1364 K. In previous studies from our laboratory, we have measured the high-temperature rate constants of seven normal and branched alkanes (n-hexane, 2-methyl-pentane, 3-methyl-pentane, 2,2-dimethyl-butane, 2,3-dimethyl-butane, 2-methyl-heptane, and 4-methyl-heptane) with OH [1] at temperatures between 880 and 1440 K. Also, the primary and secondary site-specific rate constants of H- and D- abstraction from propane and n-butane by OH were measured recently in our laboratory [28] over 840 – 1470 K.

There have been some efforts to develop rate estimation methods to describe the non-Arrhenius behavior of Fuel + OH reaction rates and to predict rate constants for fuels where experimental data are not available. Cohen [29, 30] used the group-additivity transition-state-theory (TST) method to reproduce the single-temperature measurements [20-24] of the rate constants of OH with a series of alkanes. Atkinson and co-workers [10, 31] developed another estimation method, known as the structure-reactivity relationship (SAR), to predict the reactivity of OH with various alkanes and oxygenated molecules. Recently, Sivaramakrishnan et al. [25, 26] extended these estimation methods to determine several site-specific H abstraction rate constants over a wider temperature range. Their derived rates satisfactorily reproduce the experimentally measured rate constants of OH with many alkanes including heavier molecules such as n-hexadecane. However, their site-specific rate constant expressions cannot be employed to all normal and branched alkanes because a few important site-specific rate constant expressions are not available from their work. This deficiency can be overcome by obtaining new experimental data for carefully-chosen molecules to derive additional site-specific rates.

In this work, we have measured the rate constants of the reaction of OH with 2,2-dimethyl-pentane, 2,4-dimethyl-pentane, 2,2,4-trimethyl-pentane (iso-octane) and 2,2,4,4-tetramethyl-pentane under pseudo-first-order conditions. These experiments were performed at temperatures ranging from 822 to 1367 K and pressures near 1.5 atm.

Previously measured rate constants of OH with seven large alkanes (n-hexane, 2-methyl-pentane, 3-methyl-pentane, 2,2-dimethyl-butane, 2,3-dimethyl-butane, 2-methyl-heptane, and 4-methyl-heptane) [1] are extended to lower temperatures in order to broaden the temperature validity of their Arrhenius expressions.

Finally, the rate constants of the above reactions (R1 – R11) are used to derive new site-specific rate constants for H abstraction by OH from secondary and tertiary abstraction sites. With these new site-specific abstraction rates, the rate constant of the reaction of OH with all normal and most of the branched alkanes can be calculated with high accuracy.

2. Experimental Methods

Experiments were performed in the stainless steel, high-purity, low-pressure shock tube facility (LPST) at King Abdullah University of Science and Technology (KAUST). The method and experimental setup were detailed previously [1, 28, 32, 33] and only a brief description is given here. The shock tube is made of a 9 m driver section and a 9 m driven section, with an inner diameter of 14.2

cm. The incident shock speed is measured using a series of five piezoelectric PCB pressure transducers over the last 1.3 m of the shock tube. Reflected shock temperatures and pressures are determined from the measured incident shock speed and standard shock-jump relations. Uncertainties in the calculated temperatures and pressures are approximately $\pm 0.7\%$ and $\pm 1\%$, respectively, mainly due to the uncertainty in the measured shock velocity ($\pm 0.2\%$). The facility is also equipped with a magnetically-stirred 24-litre mixing vessel and a well-furnished mixing manifold for the accurate preparation of mixtures. A double-dilution process was utilized when preparing mixtures to obtain more accurate concentrations in the mixing vessel [34].

The OH laser diagnostic and a Kistler 603B piezoelectric pressure transducer are located at a test section 2 cm from the driven section endwall. Ultraviolet light for OH absorption is generated with external frequency doubling of red light (614 nm) produced by a ring-dye cw laser that is pumped by a 10W green laser (532 nm). In the current experiments, UV light is tuned to the center (306.6868 nm) of the well-characterized $R_1(5)$ absorption line in the OH A–X (0, 0) absorption band. A common-mode-rejection scheme [35, 36] is used here which gives a detection limit of about 0.2 ppm at 1400 K and 1 atm, assuming a minimum detectable absorbance of 0.1%. The OH mole fraction is calculated from the Beer-Lambert law, $I/I_0 = \exp(-\sigma_{OH}X_{OH}PL)$, where I and I_0 are the transmitted and incident laser intensities, σ_{OH} is the OH absorption coefficient, X_{OH} is the OH mole fraction, P is the total pressure (atm), and L is the path length (14.2 cm). Estimated uncertainty in the measured OH mole fraction (X_{OH}) is approximately $\pm 3\%$, mainly due to the uncertainty in temperature and available cross-section data. Experimental data are recorded at a sampling rate of 2.5 MHz using a high-resolution (14 bit) data acquisition system.

Hydroxyl radicals were produced by rapid thermal decomposition of tert-butyl hydroperoxide (TBHP), where TBHP is known to be a clean OH precursor and has been validated in many studies [27, 33, 34, 37-42]. A 70% TBHP in water solution, 2,2-dimethyl-pentane ($\geq 99\%$), 2,4-dimethyl-pentane ($\geq$

99%), and iso-octane ($\geq 99\%$) were obtained from Sigma Aldrich while 2,2,4,4-tetramethyl-pentane ($\geq 99\%$) was purchased from VWR International. Several reflected-shock experiments were conducted for each alkane and the concentrations (alkane, TBHP) were chosen carefully based on sensitivity analyses that were based on approximate mechanism. For the experiments, alkane concentrations ranged from 128 to 163 ppm, with TBHP and water being 10 – 20 ppm and 30 – 60 ppm, respectively. The diluent was Ar, and the experiments were carried out over the temperature range 822 – 1367 K, and pressure range, 1 – 1.7 atm.

Zero-dimensional simulations with constant internal energy and volume (constant UV) constraints were performed with CHEMKIN [43]PRO commercial program. A previously published detailed chemical kinetic mechanism [44] was used to fit the experimental data for the determination of the rate constant of R3 (k_3). Three other branched alkanes studied in this work do not have published kinetic mechanisms and sub-mechanisms for their reactions with OH are developed here. The sub-mechanisms are comprised of Fuel + OH abstraction reactions and decomposition reactions of the various fuel fragments. For each fuel, the added reactions are incorporated into the base mechanism of 2-methyl-heptane developed by Sarathy et al. [45]. Additionally, a chemistry for the decomposition of TBHP and its subsequent radicals is added from Pang et al. [27].

3. Results and Discussion

3.1. High-Temperature Measurements of Alkane + OH $\rightarrow$ Products

In order to measure the rate constant of 2,2-dimethyl-pentane + OH $\rightarrow$ Products, a mixture of 158 ppm 2,2-dimethyl-pentane, 17 ppm TBHP (45 ppm of water), and balance Ar was shock-heated to a range of post-shock temperatures (822 – 1329 K). The experimentally measured OH time-histories were fitted using the sub-mechanism for 2,2-dimethyl-pentane developed here. There are four channels for 2,2-dimethyl-pentane + OH reaction:

The H-abstraction reaction rate constants of OH + 2,2-dimethyl-pentane are assumed to be similar to those of OH + 2-methyl-hexane [45] due to the similar structure of the two molecules except for the additional branching of 2,2-dimethyl-pentane. The rate constants of channels a, b, c, and d in 2,2-dimethyl-pentane system are taken to be similar to the rate constants of channels a, c, e and f in 2-methyl-hexane. Also, various products ($\text{C}_7\text{H}_{15}\text{-2-2a}$, b, c, and d) decompose according to the pathways described in the Sarathy et al. mechanism [45] for the products of 2-methyl-hexane + OH ($\text{C}_7\text{H}_{15}\text{-2a}$, b, c, d, e, and f). A similar methodology is followed to develop sub-mechanisms for 2,4-dimethyl-pentane and 2,2,4,4-tetramethyl-pentane. These sub-mechanisms are listed in Tables S1-S3 in the Supplementary Material. Also, a schematic of each molecule, highlighting the nomination of H atoms (a, b, c, and d), is given in the Supplementary Material.

The mixture composition was chosen based on OH sensitivity analysis performed for various experimental conditions. Hydroxyl radicals sensitivity is calculated as $S_{OH} = (\partial X_{OH} / \partial k_i) \times (k_i / X_{OH})$, where X_{OH} is the local OH mole fraction and k_i is the rate constant of the i^{th} reaction. The sensitivity is plotted in Fig. 1 at a representative temperature of 1023 K and shows that 2,2-dimethyl-pentane + OH is the dominant reaction. However, minor interferences from secondary reactions occur and the rate constants for the important secondary reactions are updated based on the suggestions given in ref. [33].

The branching ratios ($k_{1a \text{ or } 1b \text{ or } 1c \text{ or } 1d} / k_{\text{total}}$) at 1023 K are 0.41 for R1a, 0.227 for both R1b and R1c, and 0.136 for R1d. These branching ratios are kept unchanged when fitting the experimental profiles.

The overall rate constant ($k_1 = k_{1a} + k_{1b} + k_{1c} + k_{1d}$) is insensitive to the branching ratios because of the pseudo-first-order conditions used here. Figure 2 shows a representative raw trace of the measured OH time-history at 1023 K and 1.4 atm. The initial TBHP concentration for simulated profiles is taken from the experimental OH yield. The best-fit OH profile has a k_1 value of $1.615 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and the effect of 50% deviations from this value is also presented in Fig. 2. The rate constants for R1 (k_1), along with the experimental conditions, are listed in Table 1. Note that subscript 5 in the subsequent tables refer to the temperature and pressure conditions behind the reflected shock waves.

Detailed uncertainty analysis was performed to estimate the errors in the measured rate constant for R1 at 1023 K and 1.4 atm. Various sources of errors considered here include the temperature ($\pm 0.7\%$), mixture composition ($\pm 5\%$), OH absorption coefficient ($\pm 3\%$), wavemeter reading ($\pm 0.002 \text{ cm}^{-1}$), errors in fitting the experimental profile ($\pm 5\%$), locating time zero ($\pm 0.5 \text{ }\mu\text{s}$), and rate constants of the secondary reactions. The contribution of each of these error sources on the determination of k_1 is calculated separately. The overall uncertainty is calculated using the root-sum-squared method and is found to be $\pm 20\%$ for k_1 at 1023 K.

Fig. 1. OH sensitivity for the rate constant measurement of 2,2-dimethyl-pentane + OH at 1023 K and 1.41 atm. Initial mixture: 158 ppm 2,2-dimethyl-pentane, 17 ppm TBHP (50 ppm water), balance Ar.

Fig. 2. 2,2-dimethyl-pentane + OH reaction rate measurement at 1023 K and 1.41 atm. The best-fit simulated profile and perturbations of $\pm 50\%$ are presented.

Table 1. High-temperature rate constant data for OH + 2,2-dimethyl-pentane $\Rightarrow$ Products.

T_5 (K)	P_5 (atm)	k_1 ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
822	1.82	1.84×10^{-11}
900	1.60	2.15×10^{-11}
1002	1.56	2.59×10^{-11}
1023	1.41	2.68×10^{-11}
1161	1.50	3.31×10^{-11}
1199	1.32	3.48×10^{-11}
1270	1.75	3.82×10^{-11}
1276	1.17	3.85×10^{-11}
1329	1.13	4.48×10^{-11}

An Arrhenius plot of the rate constant of 2,2-dimethyl-pentane + OH $\Rightarrow$ products is shown in Fig. 3. Rate constants calculated from the structure-reactivity relationship (SAR) [31] estimation method are also shown as a dashed line in Fig. 3. The SAR method does a reasonable job of predicting the measured

rate constants. The curve-fit of the measured values of k_1 for the studied temperature range, shown as solid “red” line, is described by the Arrhenius expression:

$$k_1 = 1.67 \times 10^{-10} \exp(-1853 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (822 - 1329 \text{ K}) \quad (1)$$

Fig. 3. Arrhenius plot of 2,2-dimethyl-pentane + OH => products.

Similar procedures were used to measure the reaction rate constants for the reaction of OH with three other alkanes. Fuel concentrations of 163 ppm, 128 ppm, and 250 ppm were used for 2,4-dimethyl-pentane, iso-octane, and 2,2,4,4-tertamethyl-pentane, respectively. Small amounts of TBHP that insures pseudo-first-order (10 – 15 ppm) conditions were used to prepare the alkane/TBHP/Ar mixtures. Experiments were carried out over a range of temperatures for each fuel and the OH time-histories were fitted using either an existing mechanism (iso-octane [44]) or a sub-mechanism (2,4-dimethyl-pentane and 2,2,4,4-tertamethyl-pentane) developed here. Uncertainty values for k_2 , k_3 , and k_4 are estimated to be $\pm 16\%$ at 1086 K, $\pm 17\%$ at 1049 K, and $\pm 15\%$ at 1104 K, respectively. Arrhenius plots for k_2 , k_3 , and k_4 are shown in Fig. 4, Fig. 5, and Fig. 6, respectively. Predicted rate constants, using the SAR

estimation method are also shown. Among the three alkanes, only the OH + iso-octane rate constants have previously been measured at high temperatures. The rate measured by Bott and Cohen [22] at 1186 K is slightly lower than the measurements performed here (Fig. 5). The rate constants, using the Mehl et al. [44] iso-octane kinetic mechanism, underestimates the measured values by almost 40%. The SAR estimation method agrees very well with the measured OH + iso-octane rate constants. However, the modified Arrhenius expression recommended by Atkinson [9] slightly underestimates the measured OH + iso-octane rate constants. The SAR method successfully reproduces the rate constants for 2,4-dimethyl-pentane + OH (k_2) and 2,2,4,4-tetramethyl-pentane, as can be seen from Fig. 4 and Fig. 6, respectively. Measured rate constants for k_2 , k_3 , and k_4 are listed in Tables 2 – 4, and the corresponding Arrhenius expressions are:

$$k_2 = 1.52 \times 10^{-10} \exp(-1556 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (897 - 1311 \text{ K}) \quad (2)$$

$$k_3 = 2.81 \times 10^{-10} \exp(-2287 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (906 - 1367 \text{ K}) \quad (3)$$

$$k_4 = 2.00 \times 10^{-10} \exp(-1965 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (899 - 1356 \text{ K}) \quad (4)$$

Fig. 4. Arrhenius plot of 2,4-dimethyl-pentane + OH => products.

Fig. 5. Arrhenius plot of iso-octane + OH => products.

Fig. 6. Arrhenius plot of 2,2,4,4-tetramethyl-pentane + OH => products.

Table 2. High-temperature rate constant data for OH + 2,4-dimethyl-pentane => Products.

T_5 (K)	P_5 (atm)	k_2 (cm ³ molecule ⁻¹ s ⁻¹)
897	1.61	2.72×10^{-11}
902	1.61	2.74×10^{-11}
917	1.49	2.81×10^{-11}

1069	1.52	3.48×10^{-11}
1086	1.34	3.56×10^{-11}
1194	1.32	4.07×10^{-11}
1236	1.13	4.26×10^{-11}
1311	1.10	4.80×10^{-11}

Table 3. High-temperature rate constant data for OH + iso-octane => Products.

T_5 (K)	P_5 (atm)	k_3 ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
906	1.72	2.31×10^{-11}
982	1.70	2.73×10^{-11}
1049	1.60	3.13×10^{-11}
1141	1.48	3.72×10^{-11}
1228	1.39	4.32×10^{-11}
1296	1.37	4.83×10^{-11}
1367	1.33	5.40×10^{-11}

Table 4. High-temperature rate data for OH + 2,2,4,4-tetramethyl-pentane => Products.

T_5 (K)	P_5 (atm)	k_4 ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
899	1.59	2.38×10^{-11}
948	1.64	2.47×10^{-11}
1025	1.54	3.00×10^{-11}
1061	1.82	3.18×10^{-11}
1104	1.41	3.02×10^{-11}
1195	1.44	3.87×10^{-11}
1249	1.38	4.16×10^{-11}
1356	1.29	4.74×10^{-11}

3.2. Low-Temperature Rate Constant Data for Alkane + OH → Products

In this section, the current high-temperature measurements are combined with low-temperature data to generate modified Arrhenius expressions applicable over a wide temperature range. Low-temperature measurements have previously been performed for the reaction of OH with various alkanes. However, the reaction of OH with 2,2-dimethyl-pentane has not been studied previously at low temperatures [46]. The low-temperature data for k_1 is estimated here based on the fact that, at low-temperature, the rate

constants of doubly-methylated alkanes with OH are smaller when the two methyl radicals branch at the same carbon atom compared to when the two methyl radicals branch at separate carbons. This decrease in the rate constants, when doubling the branching at the same C, is evident from the reactions of pentane and hexane isomers with OH (Fig. S1 Supplementary Material). Therefore, the molecule under consideration here, 2,2-dimethyl-pentane, is expected to have smaller rate constants compared to 2,3-dimethyl-pentane (2,3-D-M-P) and 2,4-dimethyl-pentane (2,4-D-M-P). Also, the SAR estimation method does a good job of reproducing the rate constants of double CH₃ branching at the same C atom for the low-temperature reaction of OH with 2,2-dimethyl-butane and 2,2-dimethyl-propane as can be seen from Fig. S1 (Supplementary Material). We assume here that the SAR method reproduces the low-temperature rate constants of 2,2-dimethyl-pentane. The SAR calculation at low temperatures is combined with our high-temperature measurements to derive modified Arrhenius expression ($A T^b \exp^{(-E/T)} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$) for k_1 ; labeled as three-parameter fit in Fig. 7. The rate constants of 2,3 and 2,4-dimethyl-pentane with OH from Wilson et al. [47] are also shown in Fig. 7 for comparison purposes. The derived expression for k_1 is:

$$k_1 = 1.05 \times 10^{-17} T^{2.10} \exp(210.0 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (250 - 1351 \text{ K}) \quad (5)$$

Fig. 7. Arrhenius plot of 2,2-dimethyl-pentane + OH $\rightarrow$ Products over 250 – 1329 K.

For the reaction of 2,4-dimethyl-pentane with OH (k_2), the low-temperature data of Wilson et al. [47] (272 – 410 K) and Atkinson et al. [48] (297 K) are used along with the current high-temperature data to generate the three-parameter fit expression given below. The experimental data, three-parameter fit and SAR calculation are shown in Fig. 8. The temperature dependence of the rate constant k_2 is not reproduced by the SAR method at low temperatures, as can be seen from Fig. 8.

$$k_2 = 2.00 \times 10^{-16} T^{1.71} \exp(143.5 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (272 – 1311 K) (6)}$$

Fig. 8. Arrhenius plot of 2,4-dimethyl-pentane + OH $\rightarrow$ Products over 270 – 1311 K.

For the reaction of iso-octane with OH (k_3), current high-temperature data are combined with the low-temperature data of Greiner [49] (298 – 493 K) and Atkinson et al. [48] (297 K) to derive the three-parameter fit expressions given below. Experimental data and predicted rate values are presented in Fig. 9. The SAR method slightly over-predicts the low-temperature rate constant measurements. The rate constants used in the Mehl et al. [44] iso-octane kinetic mechanism underestimate the measured data at all temperatures.

$$k_3 = 7.43 \times 10^{-19} T^{2.47} \exp(397.5 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (297 – 1367 K) (7)}$$

Fig. 9. Arrhenius plot of iso-octane + OH $\rightarrow$ Products over 297 – 1367 K.

Low-temperature rate constant data are not available for the reaction of 2,2,4,4-tetramethyl-pentane with OH. Therefore, low-temperature rate constant values are estimated for this fuel, as was done for 2,2-dimethyl-pentane. There are two doubly-methylated CH_3 radicals at two carbon atoms (2 and 4) in 2,2,4,4-tetramethyl-pentane. As mentioned earlier, when double branching occurs at the same C, the OH + alkane rate constant at low temperatures is smaller compared to the case of single methyl branching. This was illustrated in Fig. 7 and Fig. S1 (Supplementary Material). To illustrate this effect for the case of a molecule with double branching at two carbons, the rate constants of OH + 2,2,3,3-tetramethyl-butane and OH + iso-octane (2,2,4-trimethyl-pentane) are compared in Fig. S2 (Supplementary Material). As expected, at low temperatures, the rate constants of 2,2,3,3-tetramethyl-butane are lower than that of iso-octane. Additionally, the SAR method successfully reproduces the low-temperature data of 2,2,3,3-tetramethyl-butane. Therefore, we assume here that the SAR method will reproduce the low-temperature rate constant data for OH + 2,2,4,4-tetramethyl-pentane (k_4). Then our measured high-

temperature data are combined with low-temperature SAR prediction to get the following modified Arrhenius expression (labeled as “three-parameter fit” in Fig. 10) for k_4 :

$$k_4 = 5.53 \times 10^{-18} T^{2.215} \exp(105.6 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (297 - 1365 \text{ K}) \quad (8)$$

Fig. 10. Arrhenius plot of 2,2,4,4-tetramethyl-pentane + OH $\rightarrow$ Products over 297 – 1365 K.

Recently, we have measured the high-temperature rate constants of seven straight and branched alkanes with OH [1]. In that work, site-specific rate constants were determined at high temperatures (900 – 1400 K). Here, we extend the applicability range of those site-specific rate constants by including low-temperature literature data for the rate constants of OH with the studied alkanes (n-hexane, 2-methyl-pentane, 3-methyl-pentane, 2,2-dimethyl-butane, 2,3-dimethyl-butane, 2-methyl-heptane, and 4-methyl-heptane).

Starting with n-hexane + OH, four different low-temperature studies are combined with the high-temperature data (881 – 1351 K) reported earlier [1]. These include the measurements of DeMore and

Bayes [50] (292 – 367 K), Donahue and Anderson [51] (300 – 390 K), Campbell et al. [52] (292 K), and Atkinson et al. [48] (297 K). All measured rate constant data are plotted in Fig. 11. The calculated rate constants using the SAR and the next-nearest-neighbor (N-N-N) [29, 30] estimation methods are also shown in Fig. 11. Also, a three-parameter fit in the form of $A T^b \exp(-E/T)$ is generated for the data shown in Fig. 11, and the following expression for k_5 is derived,

$$k_5 = 4.50 \times 10^{-18} T^{2.2} \exp(450 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (290 - 1351 \text{ K}) \quad (9)$$

This expression does a good job of fitting the experimental data across the entire temperature range, where the experimental data are within $\pm 15\%$ of the derived expression. The calculated rate constants using the SAR and N-N-N methods compare well with the measured rates for low and intermediate temperatures. The N-N-N method does a better job than SAR at high temperatures, as can be seen from Fig. 11.

Fig. 11. Arrhenius plot of $\text{n-hexane} + \text{OH} \rightarrow \text{Products}$ for the temperature range of 290 – 1351 K.

For 2-methyl-pentane, three low-temperature measurements are available in the literature. These are all single-point experiments near room temperature and include Lloyd et al. [53] (305 K), Cox et al. [54] (300 K), and Atkinson et al. [48] (297 K). These low-temperature data are used along with our previous high-temperature measurements [1] to generate the three-parameter fit expression for 2-methyl-pentane (k_6). The SAR estimation method rate constants are also shown. The derived expression is given below while the data and the fit are presented in Fig. 12.

$$k_6 = 8.60 \times 10^{-17} T^{1.8} \exp(198.2 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (297 - 1375 \text{ K}) \quad (10)$$

Fig. 12. Arrhenius plot of 2-methyl-pentane + OH $\rightarrow$ Products for the temperature range of 297 – 1375 K.

For 3-methyl-pentane, Lloyd et al. [53] (305 K) and Atkinson et al. [48] (297 K) performed single-point measurements near room temperature. Their data are used with our previous high-temperature measurements [1] to derive the three-parameter fit expression which is given below. The data and the fit along with the SAR estimation method are shown in Fig. 13.

$$k_7 = 9.75 \times 10^{-18} T^{2.1} \exp(348.4 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (297 - 1362 \text{ K}) \quad (11)$$

Fig. 13. Arrhenius plot of 3-methyl-pentane + OH $\rightarrow$ Products for the temperature range of 297 – 1362 K.

For 2,2-dimethyl-butane, Harris and Kerr [55] (245 – 328 K) and Atkinson et al. [48] (297 K) low-temperature measurements are used in conjunction with our previous high-temperature data [1] to get the three-parameter fit expression given below. The experimental data and the fit along with the SAR estimation method are shown in Fig. 14.

$$k_8 = 1.11 \times 10^{-17} T^{2.09} \exp(79.1 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (254 - 1327 \text{ K}) \quad (12)$$

Fig. 14. Arrhenius plot of 2,2-dimethyl-butane + OH $\rightarrow$ Products for the temperature range of 250 – 1327 K.

For the reaction of OH with 2,3-dimethyl-butane, low-temperature measurements of Wilson et al. [47] (290 – 407 K), Atkinson et al. [56] (299 K), Darnall et al. [57] (300 K), and Darnall et al. [58] (305 K) are used with our previous high-temperature data [1] to generate the three-parameter fit expression given below. The high- and low- temperature rate constant data, the SAR and the N-N-N estimation methods and the three-parameter fit expression are plotted in Fig. 15. As can be seen from Fig. 15, the N-N-N method does a very good job for the entire temperature range, whereas the SAR method slightly under-predicts the measured rates over the low to intermediate temperature ranges.

$$k_9 = 9.29 \times 10^{-18} T^{2.08} \exp(426.8 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (250 – 1366 K)} \quad (13)$$

Fig. 15. Arrhenius plot of 2,3-dimethyl-butane + OH $\rightarrow$ Products for the temperature range of 290 – 1366 K.

Low-temperature rate constant data are not available for the reaction of OH with 2-methyl-heptane and 4-methyl-heptane. However, a three-parameter fit expression for the wider temperature range is needed for 4-methyl-heptane to obtain the desired site-specific rates, as discussed later. In the absence of experimental data, some assumptions are used to extend the rate constants of 4-methyl-heptane to lower temperatures. Careful investigation of the n-hexane and 3-methyl-pentane (hexane isomers) low-temperature rate constant data reveals that the alkane + OH rate constants are almost identical for the isomeric singly-methylated alkane and normal alkane, as can be seen from Fig. S3 (Supplementary Material). Since 4-methyl-heptane is a symmetrical molecule just like 3-methyl-pentane, it can be assumed that the low-temperature rate constant of the symmetrical octane isomer (4-methyl-heptane) is the same as that of n-octane. Greiner [49] (296 – 497 K), Atkinson et al. [56] (299 K), Behnke et al. [59] (300 K), Koffend and Cohen [24] (1078 K), and Nolting et al. [60] (312 K) low-temperature n-octane + OH rate constant data are used in conjunction with our high-temperature rate data of 4-methyl-heptane +

OH to derive the three-parameter fit expression for k_{11} (4-methyl-heptane + OH). The relevant experimental data and the fit are shown in Fig. 16, and the three-parameter fit expression is given below:

$$k_{11} = 1.45 \times 10^{-16} T^{1.75} \exp(293.2 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (250 - 1366 \text{ K}) \quad (14)$$

Fig. 16. Arrhenius plot of 4-methyl-heptane + OH $\rightarrow$ Products rate constants for the temperature range of 296 – 1440 K.

4. Derivation of Secondary and Tertiary Site-Specific Rate Constants

Several estimation methods were developed over the years to calculate the rate constants of various molecules with OH in the absence of experimental data. The structure-reactivity relationship (SAR) of Atkinson and co-workers [10, 31] is strictly based on the group rate constants for the H-atom abstraction from primary ($-\text{CH}_3$), secondary ($-\text{CH}_2-$), and tertiary ($-\text{CH}-$) groups. In addition, these group rate constants depend on the nature of the neighboring atoms. For example, the group rate constants are expressed as $k(\text{CH}_3-\text{X}) = k_{\text{prim}}F(\text{X})$, $k(\text{X}-\text{CH}_2-\text{Y}) = k_{\text{sec}}F(\text{X})F(\text{Y})$, and $k((\text{X})(\text{Y})\text{CH}(\text{Z})) = k_{\text{tert}}F(\text{X})F(\text{Y})F(\text{Z})$, where k_{prim} , k_{sec} , and k_{tert} are the standard group rate constants for the H-atom

abstraction from primary, secondary, and tertiary groups, and $F(X)$, $F(Y)$, and $F(Z)$ are the substituent factors for the substituent groups (X , Y , and Z). The group-additivity method of Cohen [29, 30] is based on defining C–H bonds in alkanes according to next-nearest-neighbor configurations. His classification defined primary C–H bonds in alkanes as P_0 (ethane), P_1 (propane and subsequent larger alkanes), P_2 (iso-butane), and P_3 (neo-pentane) where the subscript denotes the number of C-atoms bonded to the next-nearest-neighbor C-atom of the C–H bond of interest. Similarly, various secondary (S_{ij}) and tertiary (T_{ijk}) C–H bonds can be defined using this method. Recently, Sivaramakrishnan et al. [25, 26] extended the estimation method of Cohen [29, 30] to determine three-parameter fits for several site-specific H abstraction rate constants. This was done with the aid of detailed high-level-ab-initio electronic structure theory computations of the molecular properties of reactants, products, and transition states. Their derived rates reproduced the experimental rate constants of OH with many alkanes, including heavier molecules such as n-hexadecane. However, their site-specific rate constant expressions cannot be employed to calculate rate constants of the reactions of a number of branched alkanes with OH since some important site-specific reaction rate constant expressions are not available from their work. We refer to the work of Sivaramakrishnan et al. [25, 26] by the nomination of next-nearest-neighbor (N-N-N) throughout the paper because it is based on an understanding that the primary, secondary, and tertiary C-H bonds are dependent on the number of C atoms bonded to the N-N-N carbon atom.

The SAR estimations for the reactions studied in this work are shown in Figs. 3 – 16. The SAR estimation does not agree with the experimental data very well, particularly at low temperatures where the SAR method does not reproduce the temperature dependence of the rate constants for almost all molecules except n-hexane, 2,2,-dimethyl-butane and 2,2-dimethyl-propane. Also, at high temperatures, the SAR method slightly deviates from the measured rate constants for most of the presented alkanes. In general, it is observed that SAR method successfully predicts the rate constants for doubly-methylated

molecules where the branching is at the same carbon atom, such as 2,2-dimethyl-propane, 2,2-dimethyl-butane and 2,2,3,3-tetramethyl-butane.

The N-N-N estimation method from Sivaramakrishnan et al. [25, 26] can only be applied to calculate the rate constants of n-hexane and 2,3-dimethyl-butane with OH because of the lack of several site-specific rate constant expressions. The N-N-N estimation reproduces the experimental data fairly well for n-hexane and 2,3-dimethyl-butane (Fig. 11 and Fig. 15).

Current high-temperature measurements for the rate constants of the eleven alkanes with OH ($k_1 - k_{11}$) enable us to determine rate constant expressions for a number of secondary and tertiary site-specific H abstraction rates. According to the N-N-N estimation, the rate constant of 2,2-dimethyl-butane with OH can be decomposed to the various site-specific (per-H atom) rate constants, as follows:

$$k_8 = 9P_3 + 2S_{30} + 3P_1 \quad (15)$$

where the primary abstraction rates, P_3 and P_1 , have been determined by Sivaramakrishnan et al. [25, 26]. However, S_{30} is not available and hence the rate constant k_8 cannot be estimated using this method. However, having the three-parameter fit expression of k_8 (Eq. 12) from this work allows us to determine S_{30} :

$$S_{30} = 3.35 \times 10^{-18} T^{1.97} \exp(323.1 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (250 - 1366 \text{ K}) \quad (16)$$

Following the same methodology, rate constants k_1 , k_2 , k_3 , k_4 , k_6 , k_7 , k_{10} , and k_{11} can be written in terms of the site-specific abstraction rates as follows:

$$k_1 = 9P_3 + 2S_{31} + 2S_{10} + 3P_1 \quad (17)$$

$$k_2 = 12P_2 + 2T_{100} + 2S_{22} \quad (18)$$

$$k_3 = 9P_3 + 2S_{32} + T_{100} + 6P_2 \quad (19)$$

$$k_4 = 18P_3 + 2S_{33} \quad (20)$$

$$k_6 = 6P_2 + T_{100} + 2S_{21} + 2S_{10} + 3P_1 \quad (20)$$

$$k_7 = 6P_1 + T_{101} + 4S_{20} + 3P_2 \quad (21)$$

$$k_{10} = 6P_2 + T_{100} + 2S_{21} + 2S_{11'} + 2S_{11} + 2S_{10} + 3P_1 \quad (22)$$

$$k_{11} = 6P_1 + 4S_{10} + 4S_{21} + T_{101} + 3P_2 \quad (23)$$

Rate constant expressions for S_{31} , S_{22} , S_{32} , S_{33} , T_{100} , S_{21} , T_{101} , and S_{20} are not available and will be determined here. Schematics of the molecular structures of the eleven studied alkanes, with the locations of the site-specific rate constants, are presented in Fig. S4 (Supplementary Material). Using Eq. 17 and the three-parameter fit for k_1 (Eq. 5) enables the determination of the modified Arrhenius expression for S_{31} :

$$S_{31} = 1.60 \times 10^{-18} T^2 \exp(500 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (250 - 1351 \text{ K}) \quad (24)$$

Following a similar procedure, rate constant expression for S_{33} can be calculated using Eq. 20 and the rate expression for k_4 (Eq. 8). The resulting expression is given below:

$$S_{33} = 2.83 \times 10^{-19} T^{2.25} \exp(501.3 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (250 - 1365 \text{ K}) \quad (25)$$

In order to solve the rest of the equations for the unknown site-specific rate constants, one site-specific rate constant has to be estimated to evaluate the others. By investigating the already determined site-specific rates, we decided to estimate S_{20} because there is a clear trend between S_{10} (Sivaramakrishnan and Michael [25]), S_{30} (current work) and the unknown S_{20} , as can be seen in Fig. S5 (Supplementary Material). The S_{20} rate is estimated to be the average of the known S_{10} and S_{30} rates and has the following resulting expression:

$$S_{20} = 8.49 \times 10^{-17} T^{1.52} \exp(73.4 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (250 - 1450 \text{ K}) \quad (26)$$

Once S_{20} is evaluated, T_{101} rate constant can be calculated from k_7 (Eq. 11) and Eq. 22 and has the following resulting expression:

$$T_{101} = 1.05 \times 10^{-16} T^{1.38} \exp(577.9 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (297 - 1362 \text{ K}) \quad (27)$$

The S_{21} rate constant can be calculated from k_{11} (Eq. 14) and Eq. 24 and the modified Arrhenius expression of S_{21} is given below:

$$S_{21} = 1.07 \times 10^{-15} T^{1.07} \exp(208.3 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (296 - 1440 \text{ K}) \quad (28)$$

After deriving the expression for S_{21} , T_{100} can now be calculated from k_6 (Eq. 10) and Eq. 21. The outcome is presented in terms of a modified Arrhenius expression:

$$T_{100} = 5.265 \times 10^{-15} T^{0.99} \exp(2.51 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (297 - 1375 \text{ K}) \quad (29)$$

Thereafter, S_{22} and S_{32} can be determined from k_2 and k_3 expressions, respectively. The modified Arrhenius expressions of S_{22} and S_{32} are:

$$S_{22} = 2.88 \times 10^{-13} T^{0.41} \exp(-291.5 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (272 - 1311 \text{ K}) \quad (30)$$

$$S_{32} = 9.65 \times 10^{-17} T^{1.45} \exp(180 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (297 - 1367 \text{ K}) \quad (31)$$

Table 5 lists all site-specific rate constants for H abstraction by OH from the current work and the work of Sivaramakrishnan and Michael [25]. Having these site-specific rate constants, most of the OH + n-, i-singly-methylated, i,j-doubly-methylated, i,j,k-triply-methylated, and i,j,k,l-quadruply-methylated alkane rates can be estimated using the N-N-N method, where i, j, k, and l are the positions of carbon atoms that have the methyl branching. A number of tertiary site-specific rate constants such as T_{111} , T_{120} , T_{221} , T_{222} , T_{220} , T_{330} , T_{310} , T_{333} , etc. cannot be evaluated from the current work. Determination of these remaining tertiary site-specific rate constants requires another parametric study, similar to this work, for a series of well-chosen branched alkanes.

As an example of the application and validity of the site-specific rate constants determined here, we consider the rate constant of the reaction of OH with 2-methyl-heptane. This rate can be estimated using the N-N-N method since all needed site-specific rate constants are now available. The experimental rate constants of 2-methyl-heptane from our previous measurements [1] as well as the SAR

and N-N-N estimations (current work) are presented in Fig. 17. As can be seen from Fig. 17, the N-N-N estimation method reproduces the high-temperature data very well. Although low-temperature data are not available for 2-methyl-heptane, it can be argued that the N-N-N estimation will be quite close to the real values.

Table 5. Summary of H-abstraction by OH site-specific rate constants according to the expression $A T^b \exp^{(-E/T)} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$.

Site-specific rate constant	A	b	E	Ref.
P ₀	4.47 x 10 ⁻¹⁹	2.22	373	Sivaramakrishnan and Michael [25]
P ₁	7.56 x 10 ⁻¹⁸	1.81	437	Sivaramakrishnan and Michael [25]
P ₂	9.27 x 10 ⁻¹⁹	2.08	189	Sivaramakrishnan and Michael [25]
P ₃	9.09 x 10 ⁻¹⁸	1.76	374	Sivaramakrishnan and Michael [25]
S ₀₀	1.64 x 10 ⁻¹⁷	1.75	-32	Sivaramakrishnan and Michael [25]
S ₁₀	5.86 x 10 ⁻¹⁵	0.93	254	Sivaramakrishnan and Michael [25]
S ₁₁	4.750 x 10 ⁻¹⁸	1.811	-511	Sivaramakrishnan and Michael [25]
S _{11'}	4.66 x 10 ⁻¹³	0.32	426	Sivaramakrishnan and Michael [25]
S ₂₀	8.49 x 10 ⁻¹⁷	1.52	-73.4	This work
S ₂₁	4.60 x 10 ⁻¹⁵	0.86	-142	This work
S ₂₂	2.88 x 10 ⁻¹³	0.41	291.5	This work
S ₃₀	3.35 x 10 ⁻¹⁸	1.966	-323	This work
S ₃₁	1.60 x 10 ⁻¹⁸	2.00	-500.0	This work
S ₃₂	9.65 x 10 ⁻¹⁷	1.45	-180.0	This work
S ₃₃	2.83 x 10 ⁻¹⁹	2.25	-501.3	This work
T ₀₀₀	8.04 x 10 ⁻¹⁸	1.84	-503	Sivaramakrishnan and Michael [25]

T_{100}	2.00×10^{-15}	1.19	-172	This work
T_{101}	1.05×10^{-16}	1.38	-577	This work
T_{200}	7.84×10^{-14}	0.58	-35	Sivaramakrishnan and Michael [25]

Fig. 17. Arrhenius plot of the rate constant 2-methyl-heptane + OH $\rightarrow$ Products over a temperature range of 297 – 1405 K.

5. Summary

Rate constant measurements are carried out behind reflected shock waves for OH + alkane abstraction reactions. The studied alkanes include doubly-methylated alkanes, triply-methylated alkanes, and quadruply-methylated alkanes. The rate constants are measured over 822 – 1367 K and pressures near 1.5 atm. Using current measurements and previously published rate constant data, we have derived new site-specific rate constants for H-abstraction from alkanes by OH radicals. A summary of the findings is listed here:

- We present the first high-temperature rate constant measurements for four large alkanes (2,2-dimethyl-pentane, 2,4-dimethyl-pentane, 2,2,4-trimethyl-pentane, and 2,2,4,4-tetramethyl-pentane).
- Three-parameter fits for the rate constants were developed for eleven large alkanes over a wide temperature range ($\sim 250 - 1400$ K).
- The SAR (structural reactivity approach) estimation method fails to reproduce the rate constants for most of the alkanes particularly at low temperatures.
- Nine new site-specific rate constants were derived in this work to increase validity of the N-N-N (next-nearest-neighbor) method to many other alkane + OH reactions.

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Supplementary Material

The developed sub-mechanisms for three alkanes are provided in Tables S1 – S3. Figures S1 – S3 and S5 present additional data for validation purposes. Figure S4 shows schematics of the studied alkanes and the positions of the site-specific rate constants.

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