Site-Specific Rate Constant Measurements for Primary and Secondary H- and D- Abstraction by OH Radicals: Propane and n-Butane

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Abstract

Site-specific rate constants for hydrogen (H) and deuterium (D) abstraction by hydroxyl (OH) radicals were determined experimentally by monitoring the reaction of OH with two normal and six deuterated alkanes. The studied alkanes include propane (C_3H_8), propane 2,2 D2 ($CH_3CD_2CH_3$), propane 1,1,1-3,3,3 D6 ($CD_3CH_2CD_3$), propane D8 (C_3D_8), n-butane ($n-C_4H_{10}$), butane 2,2-3,3 D4 ($CH_3CD_2CD_2CH_3$), butane 1,1,1-4,4,4 D6 ($CD_3CH_2CH_2CD_3$), and butane D10 (C_4D_{10}). Rate constant measurements were carried out over 840 – 1470 K and 1.2 – 2.1 atm using a shock tube and OH laser absorption. Previous low-temperature data were combined with the current high-temperature measurements to generate three-parameter fits, which were then used to determine the site-specific rate constants. Two primary ($P_{1,H}$ and $P_{1,D}$) and four secondary ($S_{00,H}$, $S_{00,D}$, $S_{01,H}$, and $S_{01,D}$) H- and D- abstraction rate constants, where the subscripts refer to the number of carbon (C) atoms connected to the next-nearest-neighbor (N-N-N) C atom, are obtained. The modified Arrhenius expressions for the six site-specific abstractions by OH radicals are:

$$P_{1,H} = 1.90 \times 10^{-18} T^{2.00} \exp(-340.87 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (210 - 1294 \text{ K})$$

$$P_{1,D} = 2.72 \times 10^{-17} T^{1.60} \exp(-895.57 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (295 - 1317 \text{ K})$$

$$S_{00,H} = 4.40 \times 10^{-18} T^{1.93} \exp(121.50 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (210 - 1294 \text{ K})$$

$$S_{00,D} = 1.45 \times 10^{-20} T^{2.69} \exp(282.36 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (295 - 1341 \text{ K})$$

$$S_{01,H} = 4.65 \times 10^{-17} T^{1.6} \exp(-236.98 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (235 - 1407 \text{ K})$$

$$S_{01,D} = 1.26 \times 10^{-18} T^{2.07} \exp(-77.00 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (294 - 1412 \text{ K})$$

Keywords: Shock tube; abstraction rates; propane; butane; OH absorption.

1. Introduction

Natural and liquefied petroleum gases are primarily composed of small normal and branched alkanes such as propane (C_3H_8) and butane (C_4H_{10}). Hydroxyl (OH) radical is an important reactive radical in combustion and atmospheric chemistry, and it is widely accepted that OH radical oxidation of fuels is the major oxidation route for these molecules under atmospheric and combustion conditions^{1, 2}. Despite the significant importance of this reaction from ambient to combustion temperatures, a browse through the literature, such as review articles of Atkinson^{3, 4} and the NIST Chemical Kinetics Database⁵, reveals a lack of direct rate constant measurements for OH with many small and large alkanes, particularly at high temperatures. The site/position within the fuel molecule from where H atom is being abstracted greatly influences the rate of abstraction and the branching ratios are extremely critical in determining the fuel oxidation pathways and the overall reactivity. The site-specific H-abstraction rates are termed primary (P), secondary (S), and tertiary (T) for one, two, and three hydrogen atoms bonded to the considered carbon group, respectively. Site-specific abstraction rate constant measurements are extremely rare. Theoretical calculations and/or estimation methods are generally employed to determine the site-specific reaction rates and the resulting branching ratios.

The only direct measurements of the site-specific rate constants of H- and D- abstraction by OH from alkanes were performed by Tully and co-workers⁶⁻¹¹ at low temperatures (287 – 903 K). They used a flow reactor and laser photolysis/laser induced fluorescence (LP-LIF) technique to measure H- and D- abstraction rate constants by OH from various normal, cyclic, and branched alkanes ranging from C_1 to C_8 . Subsequent to these important measurements, several theoretical/estimation methods were developed to predict these rate constants. Cohen^{12, 13} used group-additivity transition-state-theory (TST) method; Atkinson and co-workers^{14, 15} developed the structure-reactivity approach (SAR); and Sivaramakrishnan et al.^{16, 17} recently extended the next-nearest-neighbor (N-N-N) estimation method to determine three-parameter rate constant fits for several site-specific H-abstraction rate constants.

In this work, we report the first direct measurements of the rate constants of primary and secondary H- and D-abstraction by OH at higher temperatures (850 – 1400 K). This is achieved by measuring the overall rate constant for the following reactions:

Using these measurements, new site-specific rate constants for the H and D-abstraction by OH from primary and secondary C-H and C-D bonds are derived and described in the form of three-parameter expressions. The effects of the substitution of H by D in the fuel molecule on the rate constant with OH are also examined.

2. Experimental Details

Experiments were performed in a stainless steel, high-purity, low-pressure shock tube facility. The method and setup were described previously¹⁸⁻²⁰ 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. All experiments are performed behind reflected shock waves. 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 normal shock-jump relations. Uncertainties in the calculated temperature and pressure are

approximately $\pm 0.7\%$ and $\pm 1\%$, respectively. The OH laser diagnostic, along with a Kistler 603B piezoelectric pressure transducer, is located at a test section 2 cm from the driven section endwall. The shock tube facility is equipped with a magnetically-stirred 24 L mixing vessel and a well-furnished mixing manifold for preparing accurate mixtures.

The output light of a frequency-doubled ring-dye laser 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. Hydroxyl concentration is calculated from Beer-Lambert law, $I/I_0 = \exp(-k_{OH}X_{OH}PL)$, where I and I_0 are the transmitted and incident laser intensities, k_{OH} is the OH absorption coefficient, X_{OH} is the OH mole fraction, P is the total pressure (atm), and L is the optical path-length (14.2 cm). The overall estimated uncertainty in the measured OH mole fraction (X_{OH}) is approximately $\pm 3\%$, mainly due to the uncertainty in temperature and absorption coefficient.

Hydroxyl radicals are produced by rapid thermal decomposition of tert-butyl hydroperoxide (TBHP), where TBHP is known to be a clean OH precursor and has been validated previously^{18, 21-24}. A 70% TBHP in water solution from Sigma Aldrich was used in these experiments. Propane (99.99%), butane (99.99%) and research grade argon (99.999%) were supplied by AH Gases. Propane 2,2 D2 (98%), propane 1,1,1-3,3,3 D6 (98%), propane D8 (98%), butane 2,2-3,3 D4 (98%), butane 1,1,1-4,4,4 D6 (98%) were supplied by Icon Isotopes and butane D10 (98%) was purchased from C-D-N Isotopes.

Chemkin-Pro²⁵ and C₄ detailed kinetic mechanism²⁶ from Lawrence Livermore National Laboratories (LLNL) are used to perform zero-dimensional simulations with constant internal energy and volume (constant UV) assumptions. A sub-mechanism that includes specific Fuel + OH reactions TBHP chemistry¹⁸ is added to the base mechanism²⁶. Experimentally measured OH profiles are fit with simulated profiles to deduce the desired rate constants. Near pseudo-first-order conditions were maintained for all experiments performed in this work to measure the reaction rates of OH with various

alkanes. Fuel concentrations ranging from 300 to 350 ppm with 10 – 40 ppm of TBHP (30 – 90 ppm of water) diluted in argon were tested over the temperature range of 850 – 1400 K and pressures of 1.3 – 1.7 atm.

The deuterated fuels used here do not have research grade purity (> 99.5%) and hence impurities present in these fuels should be considered in the analysis of the measured reaction rate constants. Tully and co-workers⁶⁻¹¹ investigated the effect of impurities on the rate constants and found that impurities play significant role at low temperatures (~ 300 K) but have negligible effect at higher temperatures. Here, the contribution of impurities to the measurements of the rate constant of propane D8 is estimated as an example case. The deuterated fuels used in this work are certified by the supplier to have 98% purity. However, the supplier did not provide the composition of the 2% impurity. Therefore, the remaining 2% impurities are assumed to be similar to what Droege and Tully⁶ reported for a 98% pure propane D8. Their gas-chromatograph measurements resulted in the following mole fractions: 0.98 propane D8, 1.85×10^{-4} ethene D4, 3.8×10^{-5} ethane D6, 9.2×10^{-4} iso-butane, 2.59×10^{-3} butane, 5.21×10^{-3} diethyl ether, and 1.1057×10^{-2} propene D6. In order to derive the rate constant (k_4) for $C_3D_8 + OH$ from the experimental data, corrections for the reaction of OH with the impurities should be made. Therefore, k_4 is assumed to have the following expression,

$$k_4 = (k_{measured} - x_{C_2D_4}k_{C_2D_4} - x_{C_2D_6}k_{C_2D_6} - x_{i-C_4H_{10}}k_{i-C_4H_{10}} - x_{C_4H_{10}}k_{C_4H_{10}} - x_{C_4H_{10}O}k_{C_4H_{10}O} - x_{C_3D_6}k_{C_3D_6})/x_{C_3D_8} \quad (1)$$

where x_i is the mole fraction of species i in the source mixture and k_i represents the bimolecular rate constant for the reaction of species i with OH. The values of the rate constants k_i are taken from Tully and co-workers⁶. By solving Eq. (1), the ratio $k_4/k_{measured}$ comes out to be 0.9984 at 900 K, which can introduce about 0.15% error in our k_4 determination. Therefore, impurities are not analyzed further in

this work and the reported rate constants for reaction R1 to R8 are the measured rates without any corrections due to impurities.

3. Results and Discussion

3.1. Propane Isotopes + OH Rate Constants

The propane + OH rate constant measurements were carried out using 335 ppm of propane with 33 ppm of TBHP (85 ppm of water) diluted in argon at temperatures ranging from 895 to 1294 K and pressures from 1.53 to 2.14 atm. Hydroxyl sensitivity analyses were performed at various experimental conditions; a representative case is shown in Fig. 1. The OH 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 i th reaction. Propane + OH is the dominant reaction under all conditions of the current study. However, minor interferences from secondary reactions occur and the rates of the important secondary reactions are updated based on the suggestions given in¹⁸. Propane + OH has two different pathways:

The branching ratio ($k_{1a \text{ or } 1b} / k_{\text{total}}$) at 1051 K is 0.57 for R1a and 0.43 for R1b²⁶. These branching ratios are kept unchanged when fitting the experimental profiles. In fact, the determination of overall rate constant ($k_1 = k_{1a} + k_{1b}$) is insensitive to the branching ratios because of the pseudo-first-order conditions¹⁸. Figure 2 shows a representative measured OH profile at 1051 K and 2 atm. The initial TBHP concentration in the simulations is taken from the experimental OH yield. The best-fit OH profile has a k_1 value of $1.70 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ 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 tabulated in Table 1.

Fig. 1. OH sensitivity for the rate constant measurement of propane + OH at 1051 K and 2 atm. Initial mixture: 330 ppm propane, 33 ppm TBHP (85 ppm water), balance Ar.

Fig. 2. Experimental and best-fit OH profiles for propane + OH rate constant measurement. Experimental conditions are the same as Fig. 1.

Table 1. High-temperature rate constant data for propane + OH → Products.

T_5 (K)	P_5 (atm)	k_1 (cm ³ molecule ⁻¹ s ⁻¹)
895	1.59	1.17x10 ⁻¹¹
1003	1.85	1.56x10 ⁻¹¹
1006	1.57	1.49x10 ⁻¹¹
1051	2.01	1.87x10 ⁻¹¹
1060	2.14	1.65x10 ⁻¹¹
1069	1.53	1.85x10 ⁻¹¹
1070	1.31	1.69x10 ⁻¹¹
1095	2.04	1.76x10 ⁻¹¹
1108	1.86	1.81x10 ⁻¹¹
1129	1.92	1.50x10 ⁻¹¹
1137	1.94	1.70x10 ⁻¹¹
1170	1.91	2.02x10 ⁻¹¹
1231	1.94	2.24x10 ⁻¹¹
1244	1.83	2.40x10 ⁻¹¹
1294	1.65	2.73x10 ⁻¹¹

Detailed uncertainty analysis was performed to estimate the errors in the measured rate constants. Various sources of errors considered here include temperature ($\pm 0.7\%$), mixture composition ($\pm 5\%$), OH absorption coefficient ($\pm 3\%$), wavemeter reading (± 0.002 cm⁻¹), fitting the experimental profiles ($\pm 5\%$), locating time zero (± 0.5 μ s), impurities in the fuels ($\pm 2\%$), and the rate constants of the secondary reactions. The contribution of each of these error sources on the determination of k_1 is calculated separately and the overall uncertainty, calculated using the root-sum-squared method, is found to be $\pm 24\%$ for k_1 at 1051 K.

The Arrhenius plot of the rate constant of propane + OH ⇒ products is shown in Fig. 3. Our experimental data agree very well with the high-temperature data from Sivaramakrishnan et al.¹⁷. The measurements of Sivaramakrishnan et al.¹⁷ (797 – 1248 K), Bott and Cohen²⁷ (1220 K), Smith et al.²⁸ (1074 K), Bryukov et al.²⁹ (296 – 908 K), Droege and Tully⁶ (293 – 854 K), and Kozlov et al.³⁰ (210 – 480 K) are used along with our high-temperature data to produce a three-parameter fitting expression, labeled as T-P-F (Current Work) in Fig. 3. The resulting modified Arrhenius expression ($k = AT^n \exp^{(-B/T)}$) is:

$$k_1 = 7.47 \times 10^{-18} T^{2.10} \exp(-14.39 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (210 – 1294 K)} \quad (2)$$

Atkinson³ and Sivaramakrishnan et al.¹⁷ developed three-parameter fits for the available experimental rate constants of propane with OH and their expressions are also presented in Fig. 3. The three fits agree very well for the entire temperature range.

Fig. 3. Comparison of measured data with previous experimental work for propane + OH $\Rightarrow$ products.

Similar procedures were followed to measure the reaction rate constants of other propane isotopes with OH. The current measurements are the first high-temperature rate constant data for the three deuterated isotopes of propane. Mixtures containing 300 – 360 ppm fuel ($\text{CH}_3\text{CD}_2\text{CH}_3$ or $\text{CD}_3\text{CH}_2\text{CD}_3$ or C_3D_8) and 30 – 35 ppm TBHP (70 – 80 ppm water) diluted in Ar were studied behind reflected shock waves. The computed uncertainty values are $\pm 17\%$ at 1169 K, $\pm 22\%$ at 1081 K, and $\pm 18\%$ at 1122 K for k_2 , k_3 , and k_4 , respectively. The measured rate constants of propane 2,2 D2 + OH are shown in Fig. 4 along with the low-temperature data of Droege and Tully⁶. The modified Arrhenius expression of Droege and Tully⁶, developed for low temperatures, underestimates the current high-

temperature data. Therefore, a new T-P-F (three-parameter fit) for k_2 is derived in this work and is shown in Fig. 4. Similarly, T-P-F descriptions are generated for OH reaction with propane 1,1,1-3,3,3 D6 ($\text{CD}_3\text{CH}_2\text{CD}_3$) and propane D8 (C_3D_8) using the current high-temperature data and the low-temperature data of Droege and Tully⁶; these are plotted in Fig. 5 and Fig. 6. Note that the expression proposed by Droege and Tully⁶ does a good job in fitting the current high-temperature data for k_3 and k_4 . The resulting rate constant expressions for the three deuterated propanes are given below and the rate constants k_2 , k_3 , and k_4 are tabulated in Table 2, Table 3, and Table 4, respectively.

$$k_2 = 1.00 \times 10^{-16} T^{1.75} \exp(-375.07 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (290 - 1302 \text{ K}) \quad (3)$$

$$k_3 = 6.00 \times 10^{-18} T^{2.08} \exp(6.42 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (290 - 1317 \text{ K}) \quad (4)$$

$$k_4 = 1.00 \times 10^{-18} T^{2.33} \exp(-102.00 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (290 - 1341 \text{ K}) \quad (5)$$

Fig. 4. Arrhenius plot of propane 2,2 D2 + OH rate constants.

Fig. 5. Arrhenius plot of propane 1,1,1-3,3,3 D6 + OH rate constants.

Fig. 6. Arrhenius plot of propane D8 + OH rate constants.

Table 2. High-temperature rate constant data for Propane 2,2 D2 + OH → Products.

T_5 (K)	P_5 (atm)	k_2 (cm ³ molecule ⁻¹ s ⁻¹)
909	1.47	1.00×10^{-11}
974	1.49	1.25×10^{-11}
984	1.88	1.27×10^{-11}
1097	2.05	1.47×10^{-11}
1099	1.37	1.47×10^{-11}
1169	1.27	1.67×10^{-11}
1169	1.78	1.68×10^{-11}
1291	1.35	2.05×10^{-11}

1302

1.21

 2.08×10^{-11} Table 3. High-temperature rate constant data for Propane 1,1,1-3,3,3 D6 + OH $\rightarrow$ Products.

T_5 (K)	P_5 (atm)	k_3 ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
887	1.87	8.00×10^{-12}
921	1.67	9.50×10^{-12}
1027	1.62	1.11×10^{-11}
1081	1.55	1.24×10^{-11}
1166	1.52	1.46×10^{-11}
1189	1.32	1.50×10^{-11}
1289	1.29	1.72×10^{-11}
1300	1.36	1.75×10^{-11}
1317	1.23	1.88×10^{-11}

Table 4. High-temperature rate constant data for Propane D8 + OH $\rightarrow$ Products.

T_5 (K)	P_5 (atm)	k_4 ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
839	1.54	6.50×10^{-12}
893	1.73	7.00×10^{-12}
1017	1.80	1.01×10^{-11}
1020	2.01	1.02×10^{-11}
1122	1.54	1.24×10^{-11}
1146	1.84	1.30×10^{-11}
1230	1.52	1.50×10^{-11}
1269	1.46	1.60×10^{-11}
1341	1.43	1.73×10^{-11}

3.2. Butane Isotopes + OH Rate Constants

Mixtures containing 300 – 360 ppm fuel ($n\text{-C}_4\text{H}_{10}$ or $\text{CH}_3\text{CD}_2\text{CD}_2\text{CH}_3$ or $\text{CD}_3\text{CH}_2\text{CH}_2\text{CD}_3$ or C_4D_{10}) and 30 – 35 ppm TBHP (70 – 80 ppm water) diluted in Ar were tested in the shock tube to measure the rate constants for reactions R5 – R8. The methodology of getting the rate constants is the same as used for propane isotopes. Calculated uncertainties in k_5 , k_6 , k_7 , and k_8 are $\pm 16\%$ at 1133 K, $\pm 17\%$ at 1100 K, $\pm 19\%$ at 1080 K, and $\pm 17\%$ at 1122 K, respectively. For $n\text{-butane} + \text{OH}$, the rate data of Sivaramakrishnan et al.¹⁷ (823 – 1239 K), Baldwin and Walker³¹ (753 K), Hucknall et al.³² (653 K), DeMore and Bayes³³ (253 – 361 K), Droege and Tully⁸ (294 – 509 K), Talukdar et al.³⁴ (231 – 378 K),

Donahue et al.³⁵ (300 – 390 K), and Greiner³⁶ (298 – 495 K) are plotted in Fig. 7 along with our high-temperature data. Our measurements are in very good agreement with the data from Sivaramakrishnan et al.¹⁷. Atkinson³ and Sivaramakrishnan et al.¹⁷ generated three-parameter fits for butane + OH rate constants using several low- and high-temperature measurements and their derived expressions are shown in Fig. 7. The T-P-F expression from this work developed using current and all previous data, does a slightly better job of reproducing the rate constant measurements over the entire temperature range compared to the previous expressions.

Fig. 7. Arrhenius plot of butane + OH => products.

Low-temperature rate constant data are not available for the reaction of OH with butane 2,2-3,3 D4 and butane 1,1,1-4,4,4 D6. Therefore, only the current high-temperature measurements are fitted to generate the standard two-parameter Arrhenius expressions. The rate constants k_6 and k_7 are plotted in Fig. 12 for validation purposes. Two low-temperature studies by Droege and Tully⁸ (294 – 509 K) and Paraskevopoulos and Nip³⁷ (297 K) are available for the rate constants of butane D10 with OH. Due to the relatively high uncertainty of the Paraskevopoulos and Nip³⁷ data point, only the data from Droege

and Tully⁸ are used with our high-temperature data to generate the T-P-F for k_8 . The experimental data and the rate constant fits from Droege and Tully⁸ and this work are shown in Fig. 8. The three-parameter fit of Droege and Tully⁸, which was developed for their temperature range (294 – 506 K), underpredicts our high-temperature measurements. The rate constant expressions for all butane isotopes are given below. The measured rate constants k_5 , k_6 , k_7 , and k_8 are presented in Table 5, Table 6, Table 7, and Table 8.

$$k_5 = 1.00 \times 10^{-16} T^{1.76} \exp(8.41 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (230 – 1407 K)} \quad (6)$$

$$k_6 = 1.23 \times 10^{-10} \exp(-2029.00 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (885 – 1470 K)} \quad (7)$$

$$k_7 = 1.01 \times 10^{-10} \exp(-1896.00 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (901 – 1389 K)} \quad (8)$$

$$k_8 = 7.00 \times 10^{-18} T^{2.10} \exp(-47.13 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (294 – 1412 K)} \quad (9)$$

Fig. 8. Arrhenius plot of butane D10 + OH => products.

Table 5. High-temperature rate constant data for Butane + OH → Products.

T_5 (K)	P_5 (atm)	k_5 ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
909	1.55	1.80×10^{-11}
1006	2.06	2.06×10^{-11}
1037	1.66	2.12×10^{-11}

1089	1.58	2.31×10^{-11}
1133	1.45	2.47×10^{-11}
1137	1.70	2.49×10^{-11}
1252	1.42	2.94×10^{-11}
1393	2.01	3.55×10^{-11}
1407	1.73	3.65×10^{-11}

Table 6. High-temperature rate constant data for Butane 2,2-3,3 D4 + OH $\rightarrow$ Products.

T_5 (K)	P_5 (atm)	k_6 ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
886	1.56	1.31×10^{-11}
983	1.60	1.57×10^{-11}
989	1.71	1.58×10^{-11}
1100	1.37	1.90×10^{-11}
1107	1.74	1.93×10^{-11}
1183	1.29	2.17×10^{-11}
1380	1.33	2.84×10^{-11}
1470	1.66	3.17×10^{-11}

Table 7. High-temperature rate constant data for Butane 1,1,1-4,4,4 D6 + OH $\rightarrow$ Products.

T_5 (K)	P_5 (atm)	k_7 ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
901	1.61	1.24×10^{-11}
942	1.58	1.42×10^{-11}
977	1.49	1.43×10^{-11}
1080	1.33	1.70×10^{-11}
1212	1.35	2.08×10^{-11}
1260	1.16	2.23×10^{-11}
1308	1.53	2.40×10^{-11}
1389	1.18	2.64×10^{-11}

Table 8. High-temperature rate constant data for Butane D8 + OH $\rightarrow$ Products.

T_5 (K)	P_5 (atm)	k_8 ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
915	1.65	1.22×10^{-11}
954	1.60	1.32×10^{-11}
978	2.05	1.38×10^{-11}
1019	1.40	1.38×10^{-11}
1042	1.68	1.38×10^{-11}
1122	1.42	1.75×10^{-11}
1289	1.49	2.23×10^{-11}
1342	1.28	2.39×10^{-11}
1412	1.73	2.38×10^{-11}

4. Site-Specific Rate Constants

The group-additivity based transition-state-theory (TST) method developed by Cohen^{12, 13} and later refined by Sivaramakrishnan et al.^{16, 17} is implemented in this work. This method is based on an understanding that the primary and secondary C-H bonds are dependent on the number of C atoms attached to the next-nearest-neighbor (N-N-N) carbon atom. Following this methodology, the rate constants of R1 – R4 ($k_1 - k_4$) for propane isotopes + OH can be written as follows:

$$k_1 = 6P_{1,H} + 2S_{00,H} \quad (10)$$

$$k_2 = 6P_{1,H} + 2S_{00,D} \quad (11)$$

$$k_3 = 6P_{1,D} + 2S_{00,H} \quad (12)$$

$$k_4 = 6P_{1,D} + 2S_{00,D} \quad (13)$$

This linear system of equations has four unknowns ($P_{1,H}$, $P_{1,D}$, $S_{00,H}$, and $S_{00,D}$) but only three independent equations because the equality $k_1 + k_4 = k_2 + k_3 = 6P_{1,H} + 6P_{1,D} + 2S_{00,H} + 2S_{00,D}$ holds for all temperatures, as shown in Table 9 and Fig. 9. As can be seen in Table 9 and Fig. 9, the differences between the sums are fairly small and have an average deviation of 2.5% throughout the temperature range 300 – 1350 K. Note that the values for $k_1 - k_4$ are obtained from the T-P-F because measurements of the rate constants at the same temperature do not exist. These T-P-F have some uncertainties in them which are contributing to the errors reported in the equality of the rate constants presented in Table 9.

Table 9. Sums of the rate constants for number of equations reduction.

T (K)	k_1+k_4	k_2+k_3
350	2.19E-12	2.17E-12
550	6.10E-12	6.21E-12
750	1.23E-11	1.23E-11
950	2.08E-11	2.04E-11
1150	3.19E-11	3.05E-11
1350	4.56E-11	4.24E-11

Fig. 9. Sums of the rate constants (k_1+k_4 and k_2+k_3) for number of equations reduction.

An additional equation is, therefore, needed to solve for the four unknown rate constants. The value of $k_{\text{primary}} (6P_{1,H})/k_{\text{total}} (k_1)$ reported by Droege and Tully⁶ for propane is used here by extending it to high temperatures with a polynomial fit. This assumption was also used by Sivaramakrishnan et al.¹⁷ to get site-specific rates. The ratio of the two rates is:

$$\frac{k_{\text{primary}} (6P_{1,H})}{k_{\text{total}} (k_1)} = 0.704 + 0.138 \left(\frac{1000}{T} \right) + 0.004 \left(\frac{1000}{T} \right)^2 \quad (14)$$

Solving this equation with Eqs. (10) – (13) results in the following modified Arrhenius expressions for the site-specific H and D abstraction rates by OH:

$$P_{1,H} = 1.90 \times 10^{-18} T^{2.00} \exp(-340.87 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (210 - 1294 \text{ K}) \quad (15)$$

$$P_{1,D} = 2.72 \times 10^{-17} T^{1.60} \exp(-895.57 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (295 - 1317 \text{ K}) \quad (16)$$

$$S_{00,H} = 4.40 \times 10^{-18} T^{1.93} \exp(121.50 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (210 - 1294 \text{ K}) \quad (17)$$

$$S_{00,D} = 1.45 \times 10^{-20} T^{2.69} \exp(282.36 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (295 - 1341 \text{ K}) \quad (18)$$

These primary and secondary H- and D- abstraction rate constants are compared with previous determinations in Fig. 10. The D-abstraction rates were previously determined by Droege and Tully⁶ only. The primary and secondary H-abstraction rates ($P_{1,H}$ and $S_{00,H}$) from the current work agree very well with the expressions from Sivaramakrishnan et al.¹⁷ for the entire temperature range. The primary and secondary D-abstraction rate constants ($P_{1,D}$ and $S_{00,D}$) by Droege and Tully⁶ agree quite well with the current data. However, the primary and secondary H-abstraction rate constants of Droege and Tully⁶ are smaller by about a factor of 2 at temperatures higher than 800 K. We believe that our and Sivaramakrishnan et al.¹⁷ rate constant expressions are much more reliable at high temperatures. Although the primary and secondary D-abstraction rates ($P_{1,D}$ and $S_{00,D}$) from the current work generally agree with the expressions from Droege and Tully⁶, we believe that our determinations are more accurate as Droege and Tully⁶ expressions were derived only using low-temperature rate constant data.

Fig. 10. Primary and secondary H- and D- abstraction by hydroxyl from propane isotopes.

As discussed earlier, low-temperature rate constant data are not available for the reaction of OH with butane 2,2-3,3 D4 (k_6) and butane 1,1,1-4,4,4 D6 (k_7), and thus a three-parameter-fit (T-P-F) expression covering low to high temperatures cannot be obtained for these two rate constants. For n-butane (k_5) and butane D10 (k_8), T-P-F were derived in the previous section and their rate constants can be written as the linear summation of the primary and secondary abstraction rates as:

$$k_5 = 6P_{1,H} + 4S_{01,H} \quad (19)$$

$$k_8 = 6P_{1,D} + 4S_{01,D} \quad (20)$$

There are four unknowns ($P_{1,H}$, $P_{1,D}$, $S_{01,H}$, and $S_{01,D}$) in these two equations. However, according to Sivaramakrishnan et al.¹⁷, the primary H-abstraction rate constant ($P_{1,H}$) in butane is the same as that in propane and this assumption is used here. Similarly, it can be assumed that the primary D-abstraction rate constant ($P_{1,D}$) is same in propane and butane. Solving Eqs. (19) and (20), $S_{01,H}$ and $S_{01,D}$ are determined and have the following expressions:

$$S_{01,H} = 4.65 \times 10^{-17} T^{1.60} \exp(-236.98 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (235 - 1407 \text{ K}) \quad (21)$$

$$S_{01,D} = 1.26 \times 10^{-18} T^{2.07} \exp(-77.00 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (294 - 1412 \text{ K}) \quad (22)$$

These two rate constants are plotted in Fig. 11 and compared with previous determinations. Again, the secondary D-abstraction rate ($S_{01,D}$) is previously available from Droege and Tully⁸ only. The $S_{01,H}$ rate from the current work agrees well with Droege and Tully⁸ at low and intermediate temperatures and with Sivaramakrishnan et al.¹⁷ at high temperatures. This is expected since Sivaramakrishnan et al.¹⁷ fitting for k_5 (n-butane + OH) does not reproduce the low- and intermediate- temperature data very well, as was seen in Fig. 11. The $S_{01,D}$ rate from the current work agrees well with the expression derived by Droege and Tully⁸ with minor deviations at intermediate temperatures because of the different fittings of k_8 (butane D10 + OH), as was seen in Fig. 8.

Fig. 11. Secondary H- and D- abstraction by hydroxyl from butane isotopes.

The rate constants for butane 2,2-3,3 D4 (k_6) and butane 1,1,1-4,4,4 D6 (k_7) can be estimated using the N-N-N method as all needed site-specific rate constants are now known. The measured high-temperature rate constants as well as the N-N-N estimation results are presented in Fig. 12. The agreement between the estimation method and the measured k_7 is excellent at high temperatures while some deviation between the measurements and the estimation for k_6 is observed. This difference can be attributed to many reasons such as the fitting of the rate constants, especially k_8 , which directly affects the calculation of $S_{01,D}$ or the assumptions that $P_{1,H}$ and $P_{1,D}$ are the same in propane and butane. Although, the difference is not significant as the N-N-N line is within 15 – 20% of the measured data but there appears to be a systematic problem in the temperature dependency. Low-temperature measurements for k_6 and k_7 are needed to better constrain the site-specific rate constants.

Fig. 12. Measured high-temperatures rate constants for butane 2,2-3,3 D4 (k_6) and butane 1,1,1-4,4,4 D6 (k_7) along with the N-N-N estimation method: a) the high temperature range (769 – 1666 K) and b) the entire temperature range (285 – 2000 K).

5. Summary

We have conducted rate constant measurements for the reaction of OH with normal and deuterated alkanes at high temperatures. This work presents the first high-temperature rate constant measurements

for six small deuterated alkanes (propane 2,2 D2, propane 1,1,1-3,3,3 D6, propane D8, butane 2,2-3,3 D4, butane 1,1,1-4,4,4 D6, and butane D8). Using our measurements and previous low-temperature studies, six site-specific rate constants for primary and secondary H- and D- abstraction by OH are derived. These new direct measurements of the site-specific abstraction rates will aid in reducing the uncertainty in the overall Fuel + OH rate and the associated branching ratios.

6. Acknowledgements

We would like to acknowledge the funding support from Saudi Aramco under the FUELCOM program and by the Clean Combustion Research Center (CCRC) at King Abdullah University of Science and Technology (KAUST).

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Table of Contents (TOC) Image