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Site-specific reaction rate constant measurements for various secondary and tertiary H-abstraction by OH radicals

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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 → 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 (822–1367 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:

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

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

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

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

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

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

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

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

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

1. Introduction

Gasoline, diesel, and aviation fuels [2–4] are mainly composed of straight and branched large alkanes. Volatile organic compounds

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(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 C_1 to C_8) 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 (797–1259 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.

2,2-dimethyl-pentane + OH → Products (R1)

2,4-dimethyl-pentane + OH → Products (R2)

2,2,4-trimethyl-pentane(iso-octane) + OH → Products (R3)

2,2,4,4-tetramethyl-pentane + OH → Products (R4)

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.

n-hexane + OH → Products (R5)

2-methyl-pentane + OH → Products (R6)

3-methyl-pentane + OH → Products (R7)

2,2-dimethyl-butane + OH → Products (R8)

2,3-dimethyl-butane + OH → Products (R9)

2-methyl-heptane + OH → Products (R10)

4-methyl-heptane + OH → Products (R11)

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 ±0.7% and ±1%, respectively, mainly due to the uncertainty in the measured shock velocity (±0.2%). The facility is also equipped with a magnetically-stirred 24-litre mixing vessel and a well-furnished mixing manifold for

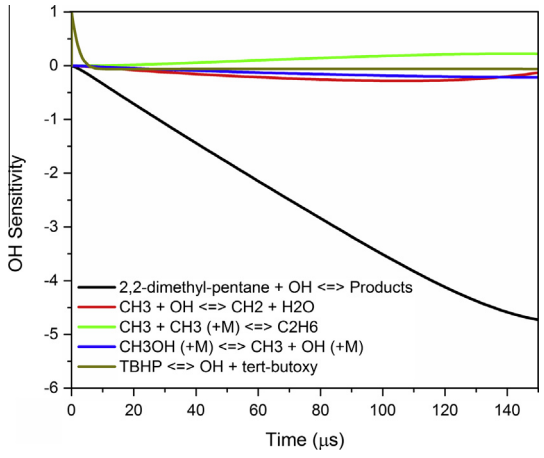

Fig. 1. OH sensitivity for the rate constant measurement of 2,2-dimethyl-pentane + OH at 1023 K and 1.41 atm. Initial mixture: 158 ppm 2,2-dimethyl-pentane, 17 ppm TBHP (50 ppm water), balance Ar.