

# Kinetic Study of OH Radical Reaction with *n*-Heptane and *n*-Hexane at 240–340K Using the Relative Rate/Discharge Flow/Mass Spectrometry (RR/DF/MS) Technique

MARY A. CRAWFORD,<sup>1</sup> BAO DANG,<sup>2</sup> JOHN HOANG,<sup>2</sup> ZHUANGJIE LI<sup>2</sup>

<sup>1</sup>Department of Chemistry, Knox College, Galesburg, IL 61401

<sup>2</sup>Department of Chemistry and Biochemistry, California State University, Fullerton, CA 92834-6808

Received 8 December 2010; revised 6 April 2011, 12 April 2011; accepted 13 April 2011

DOI 10.1002/kin.20574

Published online 20 July 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** The kinetics of reactions of OH radical with *n*-heptane and *n*-hexane over a temperature range of 240–340K has been investigated using the relative rate combined with discharge flow/mass spectrometry (RR/DF/MS) technique. The rate constant for the reaction of OH radical with *n*-heptane was measured with both *n*-octane and *n*-nonane as references. At 298K, these rate constants were determined to be  $k_{1,\text{octane}} = (6.68 \pm 0.48) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k_{1,\text{nonane}} = (6.64 \pm 1.36) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively, which are in very good agreement with the literature values. The rate constant for reaction of *n*-hexane with the OH

---

Correspondence to: Mary A. Crawford; e-mail: mcrawfor@knox.edu or Zhuangjie Li; e-mail: zli@fullerton.edu.

Contract grant sponsor: Howard Hughes Medical Institute.

Contract grant number: HHMI 52005130.

Contract grant sponsor: Knox College Faculty Research Funds.

Contract grant sponsor: National Science Foundation.

Contract grant number: NSF CHE 0354159.

Contract grant sponsor: CSU Special Fund for Research, Scholarship, and Creative Activity Minigrant.

Contract grant sponsor: Untenured Faculty Supports Grants of CSUF.

© 2011 Wiley Periodicals, Inc.

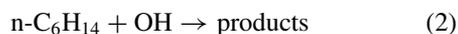
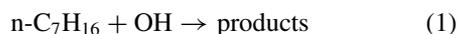
radical was determined to be  $k_2 = (4.95 \pm 0.40) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298K using *n*-heptane as a reference. The Arrhenius expression for these chemical reactions have been determined to be  $k_{1,\text{octane}} = (2.25 \pm 0.21) \times 10^{-11} \exp[(-293 \pm 37)/T]$  and  $k_2 = (2.43 \pm 0.52) \times 10^{-11} \exp[(-481.2 \pm 60)/T]$ , respectively. © 2011 Wiley Periodicals, Inc. Int J Chem Kinet 43: 489–497, 2011

## INTRODUCTION

The important role of hydroxyl (OH) radical in the removal of volatile organic compounds (VOCs) from the atmosphere is well studied [1]. In the troposphere, VOCs can also be transformed by reaction with nitrate (NO<sub>3</sub>) radicals, atomic chlorine (Cl), and ozone (O<sub>3</sub>), and by photolysis (at wavelength  $\geq 290 \text{ nm}$ ) [2]. However, it is the oxidation of VOCs by OH radicals in the atmosphere that serves as the primary removal channel of VOC pollutants in both remote and polluted atmospheres [1]. Nonmethane hydrocarbons (NMHCs) are an important class of VOCs [3,4] emitted into the atmosphere by both anthropogenic and biogenic sources [5]. Kinetic study for reactions of OH with NMHCs is therefore important for a better understanding of NMHCs atmospheric chemistry and their contribution to air pollution and air quality deterioration.

Two NMHC's of interest are *n*-heptane and *n*-hexane. Both compounds are derived from petroleum, and are used as industrial solvents. Heptane is commonly used in the testing of gasoline engine knock [6], and hexane is widely used as a replacement for mercury in low-temperature thermometers and for extraction purposes in the oil seed processing industry [6].

Under ambient conditions numerous studies have reported the reaction rate coefficients of OH radicals with *n*-heptane and *n*-hexane,



[2,3,7–23]. There is a good agreement in previous kinetics investigation for the reaction of *n*-heptane with hydroxyl radical at or near room temperature, with a rate constant ranging between  $k_1 = (6.34\text{--}7.31) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , and the recommended room temperature rate constant of this reaction is  $k_1 = 6.76 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [2]. Similarly, there is an excellent agreement in the room temperature rate constant for the reaction of hydroxyl radical with hexane over a temperature range of 292–305K in previous studies. A rate constant of  $k_2 = (5.1\text{--}6.0) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  had been reported for this reaction and the recommended room temperature rate constant is  $k_2 = 5.20 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [2]. There

are also a few kinetic investigations for reactions 1 and 2 as a function of temperature above room temperature. Koffend and Cohen [3] studied reactions 1 and 2 at 1086K using the Shock heating/Resonance absorption (SH/RA) technique. Donahue et al. [20] studied the reaction of *n*-hexane with hydroxyl radical at 300–390K using a high-pressure flow system. More recently, DeMore and Bayes [22] used the relative rate technique to study the reaction over a temperature range of 292–397K, and their kinetic results are in good agreement with that of Donahue et al. However, previous temperature-dependent studies of the reaction of OH with *n*-hexane and *n*-heptane have not been carried out at temperatures representative of the troposphere. As a result, the temperature-dependent behavior of these reactions under tropospheric conditions has not been well established [2]. In this paper, we report a kinetics study of reactions 1 and 2 over the temperature range of 240–340K using the combination of the relative rate with the discharge flow/mass spectrometry technique (RR/DF/MS), in which both *n*-octane and *n*-nonane were used as reference compounds for determining the rate constant of *n*-heptane reaction with OH at 298K. Normal octane was also used for examining the temperature dependence of the rate constant for this reaction at 240–340K. The rate constant for the reaction of OH radicals with *n*-hexane at 240–340K was determined in the present work using *n*-heptane as a reference.

## EXPERIMENTAL

The RR/DF/MS experimental setup has been described elsewhere [24,25] and hence will only be briefly discussed here. The flow reactor system consists of a 100 cm long Pyrex tube with a 5.08 cm-i.d. and a double sliding injector made of two concentric Pyrex tubes with an internal diameter of 7 mm and 12.7 mm, respectively. A Teflon sheet was placed inside the reactor to reduce OH wall loss. The inner sliding injector of the double sliding injector was coated with halocarbon wax (series 1500; Halocarbon Products Corp.) to reduce the loss of atomic fluorine due to the interaction between the fluorine atoms and the Pyrex surface of the injector. The vacuum chamber housing a quadrupole mass spectrometer was a two-staged

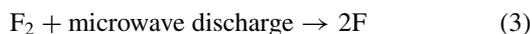
differentially pumped vacuum system that utilizes two 6-inch diffusion pumps with liquid nitrogen baffles. The ultimate vacuum in the second stage was  $<5 \times 10^{-10}$  Torr. A 125 cfm mechanical pump (Edwards Model E2M175) was employed to maintain a steady-state pressure of approximately 1 Torr in the reactor. A removable liquid nitrogen trap was placed downstream of the reactor outlet to protect the vacuum pump from corrosive reactants and products. Helium was used as the carrier gas and was admitted into the flow reactor through both the sliding injector and a sidearm inlet port located upstream of the reactor. A flow of helium and reactant mixture with a total flow rate of 1600–1700 standard cubic centimeter per minute (sccm) was introduced into the flow reactor, resulting in a flow velocity of about  $1000 \text{ cm s}^{-1}$ . For a sliding injector moving distance of 35 cm, the corresponding gaseous residence time in the reactor was about 35 ms.

Continuous sampling at the downstream end of the flow tube, through a two-stage beam inlet system, allowed mass spectrometric detection and quantification of reactants and products. The mass spectrometer (Extrel Model Max 1000) has an electron impact ionization source that emits bombarding electrons with 40 eV of impact energy for the ionization of both reactants and products. Gaseous samples of reactants were introduced into the mass spectrometer in a stream of molecules created when the gaseous mixture passed through a pinhole from the flow reactor. Beam modulation was accomplished with a 200 Hz tuning fork chopper placed inside the second stage of the mass spectrometer. In the present study, *n*-hexane, *n*-heptane, *n*-octane, and *n*-nonane molecules were identified by the mass spectroscopic detection of their parent ion at  $m/z = 86, 100, 114, \text{ and } 128$ , respectively, and the decay of both the target (*n*-hexane or *n*-heptane) and the reference (*n*-heptane, *n*-octane, or *n*-nonane) was monitored as a function of the initial concentration of the hydroxyl radical at a fixed reaction time of 35 ms. It was found that the *n*-octane, and *n*-nonane molecules did not produce daughter fragments at  $m/z = 86$  and 100 and the *n*-heptane molecule did not produce a daughter fragment at  $m/z = 86$ . It was also found on the basis of our experimental observations that the products from the reactions of OH radicals with *n*-hexane and *n*-heptane did not yield a species giving rise to a signal at  $m/z = 86$  and 100, respectively. The signals at  $m/z = 86$  and 100 were therefore unique to *n*-hexane and *n*-heptane, respectively, and there was no interference involved in simultaneous mass spectroscopic detection of target and reference compounds in the present work.

Ion signals from the MS channeltron detector were sent to a lock-in amplifier (SR510) that was referenced to the chopper frequency. The analog signals were then

converted to digital form (Analog Devices RTI/815) and recorded on a microcomputer.

Hydroxyl radicals were produced in the double sliding injector by reacting  $\sim 7 \times 10^{14}$  molecules  $\text{cm}^{-3}$  of water vapor, carried by 100 sccm of He, with fluorine atoms generated upstream of the double sliding injector by microwave discharge of 5%  $\text{F}_2$  balanced in helium,



$$k_4(298\text{K}) = 1.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

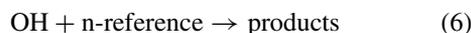
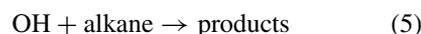
[26]. The  $\text{F}_2$  was carried by 1500 sccm of He.

Both the target and the reference compounds were carried each by 200 sccm of He, and introduced into the flow reactor from the sidearm inlet port. They were mixed prior to entering the reactor to ensure that they shared the same exposure time toward the OH radicals.

Helium (>99.999%) was obtained from Oxygen Service Company (Orange, CA) and  $\text{F}_2$  (5% in Helium) is obtained from Spectra Gases (Stewartville, NJ). All gases were used as received. The alkanes, *n*-heptane (99.95%), *n*-hexane (99.97%), and *n*-octane (>99%) were obtained from Aldrich Chemical Company, Inc. (St. Louis, MO), and *n*-nonane (>99%) was obtained from Chevron Phillips Chemical Company (Woodlands, TX). The alkanes were degassed via freeze-thaw cycles prior to their usage. Deionized water was used as the OH precursor.

## RESULTS AND DISCUSSION

According to the kinetic formulation of the RR/DF/MS technique [24], decay data of a target compound (i.e., *n*-hexane or *n*-heptane) and a reference compound are collected in the presence of hydroxyl radical. Assuming that both the target and the reference compounds reacted only with the hydroxyl radical via



it could be shown that [24]

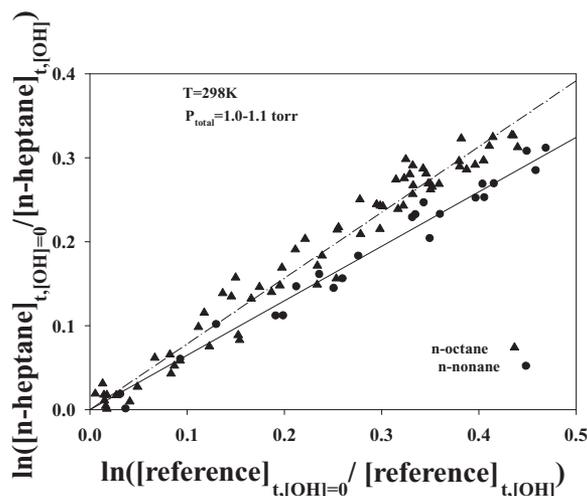
$$\begin{aligned} & \ln([\text{alkane}]_{t, [\text{OH}] = 0} / [\text{alkane}]_{t, [\text{OH}]}) \\ & = (k_5/k_6) \ln([\text{reference}]_{t, [\text{OH}] = 0} / [\text{reference}]_{t, [\text{OH}]}) \quad (I) \end{aligned}$$

where  $[\text{alkane}]_{t, [\text{OH}] = 0}$  and  $[\text{reference}]_{t, [\text{OH}] = 0}$  represent the concentrations of the alkane and the reference compounds, respectively, in the absence of OH

radicals at a fixed reaction time  $t$ . Similarly,  $[\text{alkane}]_{t,[\text{OH}]}$  and  $[\text{reference}]_{t,[\text{OH}]}$  represent the concentrations of the alkane and reference compounds in the presence of OH radicals at time  $t \cdot k_5$  and  $k_6$  are rate constants for reactions 5 and 6, respectively. Thus a straight line with a slope equal to  $k_5/k_6$  is expected when plotting  $\ln([\text{alkane}]_{t,[\text{OH}]=0}/[\text{alkane}]_{t,[\text{OH}]})$  versus  $\ln([\text{reference}]_{t,[\text{OH}]=0}/[\text{reference}]_{t,[\text{OH}]})$ . The  $k_5$  is calculated using  $k_6$  at the conditions probed in the experiment. Repeating the above procedure at various temperatures allows determination of a rate constant as a function of temperature for reactions 1 and 2.

### *n*-Heptane + OH

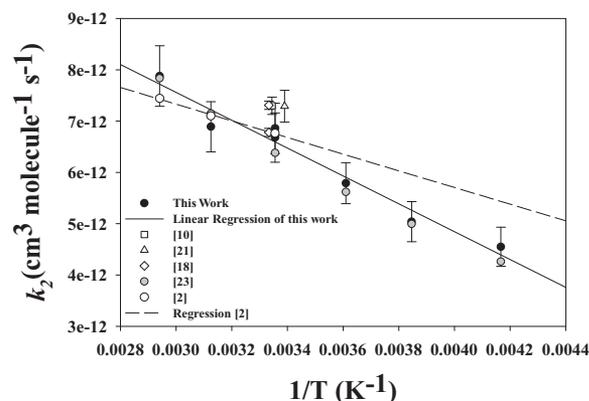
Typical kinetic data of *n*-heptane + OH versus *n*-octane + OH and *n*-heptane + OH versus *n*-nonane + OH at 298K are shown in Fig. 1. The data were collected at  $298 \pm 2\text{K}$  and a total pressure of  $\sim 1$  Torr in the flow reactor. The OH radical concentration was controlled by regulating the amount of  $\text{F}_2$  ( $(0\text{--}2) \times 10^{13}$  molecule  $\text{cm}^{-3}$ ) passing through the microwave discharge cavity. The dissociation efficiency of  $\text{F}_2$  was found to be in the range of 95%–100% depending on the initial amount of  $\text{F}_2$  added into the reactor. Figure 1 shows that the decay of both *n*-heptane and the target compounds follow the relationship predicted by equation (1) over a concentration range of 0%–40% loss of



**Figure 1** Kinetic data acquired with the RR/DF/MS technique for the reaction of *n*-heptane with OH radicals at 298K and a fixed reaction time of 35 ms using *n*-octane (filled triangle) and *n*-nonane (filled circle) as reference compounds. The experiments are carried out at a total pressure of 1.0–1.1 Torr. Initial concentrations were  $(3.65\text{--}6.51) \times 10^{13}$ ,  $(5.11\text{--}5.83) \times 10^{13}$ , and  $(3.59\text{--}4.04) \times 10^{13}$  molecules  $\text{cm}^{-3}$  for *n*-heptane, *n*-octane, and *n*-nonane, respectively. The OH concentration was varied in a range of  $(0\text{--}9.4) \times 10^{13}$  molecules  $\text{cm}^{-3}$ .

reactants. A linear regression of all experimental data points produced rate constant ratios of  $k_1/k_{n\text{-octane}} = 0.788 \pm 0.016$  (a total of 75 data points) and  $k_1/k_{n\text{-nonane}} = 0.685 \pm 0.015$  (a total of 28 data points), respectively. The error bar reported here are due to the standard deviation of the slopes. Using the rate constants of  $k_{6,n\text{-octane}} = (8.48 \pm 0.61) \times 10^{-12}$   $\text{cm}^3$  molecule $^{-1}$   $\text{s}^{-1}$  previously determined in this lab [25] and  $k_{6,n\text{-nonane}} = (9.70 \pm 1.94) \times 10^{-12}$   $\text{cm}^3$  molecule $^{-1}$   $\text{s}^{-1}$  recommended for the reaction of the hydroxyl radical with *n*-nonane [2], respectively, the rate constants for reaction 1 was determined to be  $k_{1,\text{octane}} = (6.68 \pm 0.48) \times 10^{-12}$   $\text{cm}^3$  molecule $^{-1}$   $\text{s}^{-1}$  and  $k_{1,\text{nonane}} = (6.64 \pm 1.36) \times 10^{-12}$   $\text{cm}^3$  molecule $^{-1}$   $\text{s}^{-1}$  at 298K, respectively. The error bar reported here was taken as  $2\sigma$ , which took into account the scatter of the data fitting, as well as the experimental uncertainties such as temperature, pressure, flow rate, and the concentration of both target and reference compounds.

To assess the accuracy of our kinetics measurement, model simulation calculations were also performed to investigate the potential effects of atomic oxygen and atomic hydrogen, which could be produced from secondary reactions in our chemical system, on the decay of the target and reference compounds via a chemical reaction scheme shown in Table I. The model used the fourth-order Runge-Kutta method to numerically solve differential equations providing concentration of chemical species of interest as a function of time [32]. Using initial concentrations of about  $1.5 \times 10^{14}$  molecule  $\text{cm}^{-3}$  for the target and  $6 \times 10^{13}$  molecule  $\text{cm}^{-3}$  for the reference compounds and an initial concentration of about  $9 \times 10^{13}$  molecule  $\text{cm}^{-3}$  for the OH radical, respectively, our simulation



**Figure 2** Arrhenius plot for the reaction of *n*-heptane + OH at 240–340K along with available experimental data in the literature. The dotted line generated over the temperature range of the current work using the recommended Arrhenius expression in [2]. Calculated data using the Arrhenius expression in [23] are also included for comparison.

**Table I** Reaction Scheme for Chemical Model Simulation to Assess the Effect of Atomic Oxygen and Atomic Hydrogen on the Decay of Target and Reference Compounds in RR/DF/MS Kinetic Data Analysis

Reaction <sup>a</sup>	k (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	Reference
F + H <sub>2</sub> O → HF + OH	1.4 × 10 <sup>-11</sup>	[26]
OH + OH → H <sub>2</sub> O + O	1.9 × 10 <sup>-12</sup>	[26]
OH + wall → product	10 <sup>b</sup>	Estimated [35] <sup>c</sup>
O + F <sub>2</sub> → FO + F	1.0 × 10 <sup>-16</sup>	[27]
FO + OH → O <sub>2</sub> + HF	1.3 × 10 <sup>-12</sup>	Estimated <sup>d</sup>
H + F <sub>2</sub> → HF + F	1.38 × 10 <sup>-12</sup>	[28]
O + OH → O <sub>2</sub> + H	3.3 × 10 <sup>-11</sup>	[26]
H + wall → product	10 <sup>b</sup>	Estimated [35] <sup>c</sup>
H + OH + M → H <sub>2</sub> O + M	2.3 × 10 <sup>-31e</sup>	[29]
<i>n</i> -C <sub>6</sub> H <sub>14</sub> (hexane) + OH → products	4.89 × 10 <sup>-12</sup>	This work
<i>n</i> -C <sub>7</sub> H <sub>16</sub> (heptane) + OH → products	6.52 × 10 <sup>-12</sup>	This work
O + <i>n</i> -C <sub>6</sub> H <sub>14</sub> → OH + other products	6.62 × 10 <sup>-14</sup>	[30]
O + <i>n</i> -C <sub>7</sub> H <sub>16</sub> → OH + other products	1.19 × 10 <sup>-13</sup>	[31]
H + <i>n</i> -C <sub>6</sub> H <sub>14</sub> → H <sub>2</sub> + other products	5.80 × 10 <sup>-15</sup>	Estimated [36] <sup>f</sup>
H + <i>n</i> -C <sub>7</sub> H <sub>16</sub> → H <sub>2</sub> + other products	5.80 × 10 <sup>-15</sup>	Estimated [36] <sup>f</sup>

<sup>a</sup>Initial concentrations are [F<sub>2</sub>]<sub>0</sub> = 2.4 × 10<sup>12</sup>, [H<sub>2</sub>O]<sub>0</sub> = 7.0 × 10<sup>14</sup>, [OH]<sub>0</sub> = 9.0 × 10<sup>13</sup>, [*n*-C<sub>6</sub>H<sub>14</sub>]<sub>0</sub> = 1.5 × 10<sup>14</sup>, and [*n*-C<sub>7</sub>H<sub>16</sub>]<sub>0</sub> = 6 × 10<sup>13</sup> molecules cm<sup>-3</sup>, respectively. The initial concentrations of all other species are set to zero.

<sup>b</sup>The unit is s<sup>-1</sup> for the wall loss process.

<sup>c</sup>Estimate based on OH wall loss.

<sup>d</sup>Estimate based on *k*(ClO + OH).

<sup>e</sup>The unit is cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>.

<sup>f</sup>Estimate based on H + *n*-C<sub>4</sub>H<sub>10</sub>.

**Table II** Summary of Rate Constant (in cm<sup>3</sup> Molecule<sup>-1</sup> s<sup>-1</sup>) for the Reaction of Hydroxyl Radical with *n*-Heptane, *k*<sub>1</sub>, at 240–340K

T (K)	Reference Compound	Slope <sup>a</sup>	<i>k</i> <sub>1</sub> (×10 <sup>12</sup> )	P <sub>total</sub> (Torr)	Technique <sup>b</sup>	Reference
240	<i>n</i> -octane	0.680 ± 0.013 (53)	4.55 ± 0.38	1.0–1.1	RR/DF/MS	This work
260	<i>n</i> -octane	0.708 ± 0.011 (72)	5.04 ± 0.39	1.0–1.1	RR/DF/MS	This work
277	<i>n</i> -octane	0.732 ± 0.014 (45)	5.79 ± 0.40	1.00–1.1	RR/DF/MS	This work
298	<i>n</i> -octane	0.788 ± 0.016 (75)	6.68 ± 0.48	1.0–1.1	RR/DF/MS	This work
320	<i>n</i> -octane	0.796 ± 0.022 (55)	6.89 ± 0.49	1.0–1.1	RR/DF/MS	This work
340	<i>n</i> -octane	0.810 ± 0.018 (55)	7.88 ± 0.59	1.0–1.1	RR/DF/MS	This work
298	<i>n</i> -nonane	0.685 ± 0.015 (28)	6.64 ± 1.36	1.0–1.1	RR/DF/MS	This work
298	<i>n</i> -hexane	n/a	6.48	760	RR/GC/FID	[23]
298	<i>n</i> -hexane	n/a	6.52	760	RR/GC/FID	[23]
298	cyclohexane	n/a	6.24	760	RR/GC/FID	[23]
298	cyclopentane	n/a	6.36	760	RR/GC/FID	[23]
299 ± 2	<i>n</i> -hexane	1.28 ± 0.02	7.30 ± 0.17	735	RR/GC/FID	[10]
295 ± 2	<i>n</i> -octane	n/a	7.29 ± 0.31	750	RR	[21]
300 ± 3	<i>n</i> -octane	n/a	7.31 ± 0.08	n/a	RR	[18]
300	<i>n</i> -octane	n/a	6.78 ± 0.08	n/a	RR	[16]
1186	n/a	n/a	33.4	n/a	SH-RA	[3]

<sup>a</sup>The error bar is taken as 2σ and the number in the parentheses represents the data points collected at corresponding temperature.

<sup>b</sup>RR: relative rate; GC: gas chromatography; DF: discharge flow; MS: mass spectrometry; FID: flame ionization detection; LIF: laser induced fluorescence; SH: shock heat; RA: resonance absorption.

results predicted that in 35 ms of reaction time in the flow tube more than 99.9% of the OH radicals are removed and less than 1% of the target and reference compounds can be consumed by reactions with atomic oxygen and atomic hydrogen. This indicates that these reactions have very little effect on the decay of the

target and reference compounds, and hence one could conclude with a high degree of certainty that the decay of both target and reference compounds was due to their reaction with the OH radicals.

The effect of the alkyl radicals formed from the reaction of OH + target and OH + reference on each

of their concentrations are expected to be small based on our previous OH + C<sub>8</sub>-C<sub>10</sub> *n*-alkane work, which showed that the products from the OH + *n*-alkane reaction had little effect on the 1,4-dioxane or diethyl ether mass spectral intensity (<3.5%) [25].

The rate constant for reaction 1 at various temperatures along with available literature kinetic data for the same reaction are summarized in Table II and Fig. 2. The room temperature rate constants determined in the present work are in excellent agreement with previous results of  $k_1 = (6.34\text{--}7.31) \times 10^{-12} \text{ cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1}$  utilizing different techniques and reference compounds [11,16,18,21,23]. As shown in Table II and Fig. 2, the rate constant for reaction 1 was found to increase with temperature over a temperature range of 240–340K. An Arrhenius expression was then derived

using the kinetic data in Table II to be  $k_1 = (2.25 \pm 0.14) \times 10^{-11} \exp[(-293 \pm 37)/T]$ , which has an A factor and E/R value that fall somewhere in between those Arrhenius expressions of  $k_1 = (3.38 \pm 0.17) \times 10^{-11} \exp[(-497 \pm 16)/T]$  reported by Wilson et al. [23] and of  $k_1 = (1.28 \pm 0.21) \times 10^{-11} \exp[(-190)/T]$  recommended by Atkinson [2], respectively. Nevertheless, our  $k_1$  values are very consistent with that reported by Wilson et al. [23] as illustrated in Fig. 2. The activation energy of reaction 1 is then determined to be  $E_{a,1} = (0.58 \pm 0.05) \text{ kcal mole}^{-1}$  accordingly.

### *n*-Hexane + OH

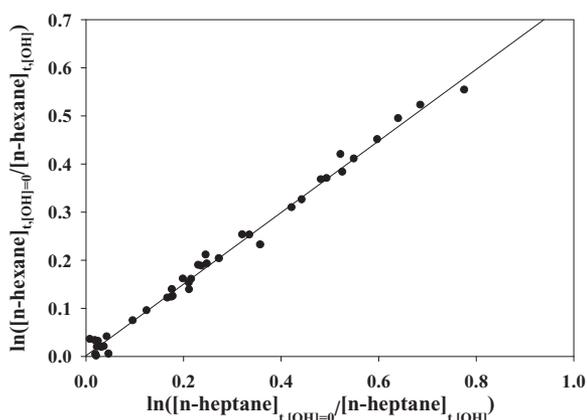
Kinetic data set acquired at 298K using the RR/DF/MS technique is shown in Fig. 3. It can be seen from Fig. 3

**Table III** Summary of Rate Constant (in  $\text{cm}^3 \text{ Molecule}^{-1} \text{ s}^{-1}$ ) for the Reaction of Hydroxyl Radical with *n*-Hexane,  $k_2$

T (K)	Reference Compound	Slope <sup>a</sup>	$k_2 (\times 10^{12})$	P <sub>total</sub> (Torr)	Technique <sup>b</sup>	Reference
240	<i>n</i> -heptane	0.70 ± 0.02 (28)	3.19 ± 0.27	1.0–1.1	RR/DF/MS	This work
260	<i>n</i> -heptane	0.73 ± 0.01 (35)	3.68 ± 0.29	1.0–1.1	RR/DF/MS	This work
277	<i>n</i> -heptane	0.80 ± 0.02 (25)	4.63 ± 0.32	1.00–1.1	RR/DF/MS	This work
298	<i>n</i> -heptane	0.75 ± 0.01 (65)	5.00 ± 0.29	1.0–1.1	RR/DF/MS	This work
320	<i>n</i> -heptane	0.73 ± 0.01(38)	5.03 ± 0.36	1.0–1.1	RR/DF/MS	This work
340	<i>n</i> -heptane	0.75 ± 0.02 (31)	5.91 ± 0.44	1.0–1.1	RR/DF/MS	This work
240	n/a	n/a	3.52	760	RR/GC	[22]
260	n/a	n/a	4.1	760	RR/GC	[22]
277	n/a	n/a	4.6	760	RR/GC	[22]
305 ± 2	<i>n</i> -butane	n/a	5.1 ± 1.1	n/a	RR	[7]
303	<i>cis</i> -2-butene	n/a	6.0	n/a	RR	[8]
292	<i>n</i> -butane	n/a	5.6 ± 0.8	n/a	RR	[9]
299 ± 2	<i>n</i> -butane	n/a	5.23 ± 0.09	n/a	RR	[10]
298 ± 2	propene	n/a	5.55 ± 0.20	n/a	RR	[11]
295	propene	n/a	5.21 ± 0.47	0.98	RR/GC/FID	[12]
295	<i>n</i> -butane	n/a	5.17 ± 0.52	n/a	RR	[13]
295	n/a	n/a	5.11	760	RR/GC	[22]
300	toluene	n/a	6.2	n/a	RR	[14]
300	ethene	n/a	5.91 ± 0.68	n/a	RR	[15]
300	<i>n</i> -butane	n/a	5.20	n/a	RR	[16]
312	<i>n</i> -heptane	n/a	5.75 ± 0.56	n/a	RR	[17]
298	<i>n</i> -ethane	n/a	5.19	760	RR/GC/FID	[22]
298	<i>n</i> -pentane	n/a	5.53 ± 1.55	1.01	RR/GC/FID	[19]
300	<i>n</i> -octane	n/a	5.68 ± 0.04	n/a	RR	[18]
300	n/a	n/a	5.45 ± 0.16	30	DF/LIF	[20]
320	n/a	n/a	5.8	760	RR/GC/FID	[21]
325	n/a	n/a	6.11 ± .18	30	DF/LIF	[20]
340	n/a	n/a	6.23 ± .19	30	DF/LIF	[20]
340	n/a	n/a	6.34	760	RR/GC/FID	[12]
360	n/a	n/a	6.43 ± .45	30	DF/LIF	[20]
375	n/a	n/a	7.33 ± 0.62	30	DF/LIF	[20]
390	n/a	n/a	7.29 ± 0.22	30	DF/LIF	[20]
962	n/a	n/a	21.8	n/a	SH-RA	[3]

<sup>a</sup>The error bar is taken as 2σ and the number in the parentheses represents the data points collected at corresponding temperature.

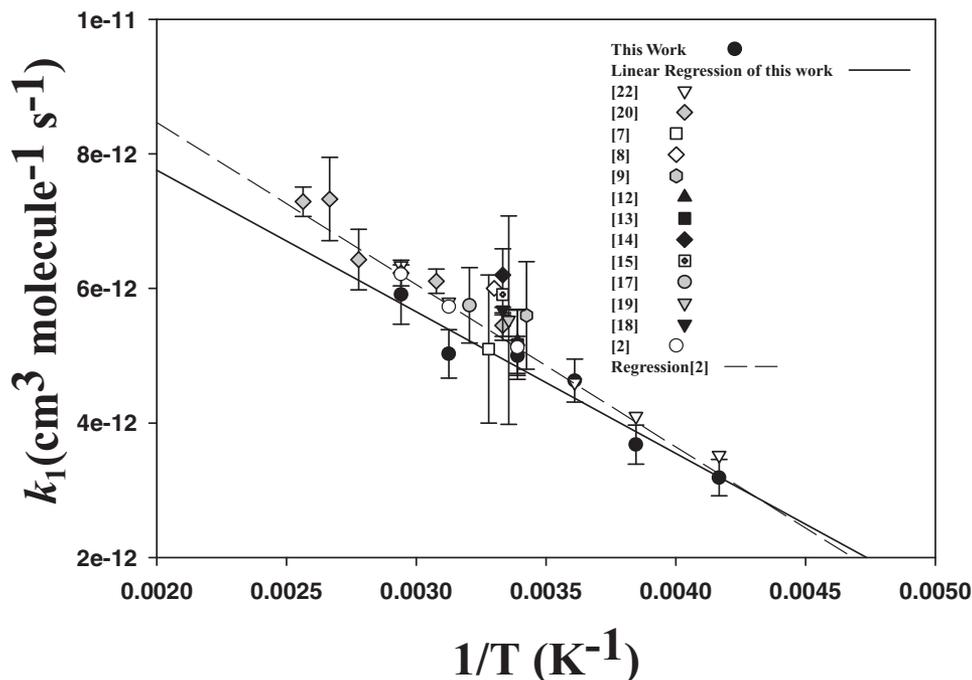
<sup>b</sup>RR: relative rate; GC: gas chromatography; DF: discharge flow; MS: mass spectrometry; FID: flame ionization detection; LIF: laser induced fluorescence; SH: shock heat; RA: resonance absorption.



**Figure 3** Kinetic data acquired with the RR/DF/MS technique for the reaction of *n*-hexane with OH radicals at 298K and a fixed reaction time of 35 ms using *n*-heptane as reference compound. The experiments are carried out at a total pressure of 1.0–1.1 Torr. Initial concentrations were  $(2.47\text{--}3.57) \times 10^{13}$  and  $(3.55\text{--}3.78) \times 10^{13}$  molecules  $\text{cm}^{-3}$  for *n*-hexane and *n*-heptane, respectively. The OH concentration was varied in a range of  $(0\text{--}9.4) \times 10^{13}$  molecules  $\text{cm}^{-3}$ .

that the kinetic data could also be well described by Eq. (1). Linear regression of the data in Fig. 3 produced a rate constant ratio of  $k_2/k_1 = 0.75 \pm 0.01$ . Using the average value of  $k_2 = (6.66 \pm 0.39) \times 10^{-12}$

$\text{cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1}$ , a value of  $k_2 = (5.00 \pm 0.29) \times 10^{-12} \text{ cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1}$  was derived at 298K for the reaction of *n*-hexane with OH radicals. The  $k_2$  value determined in the present work is in good agreement with previous room temperature  $k_2$  values [2,22] summarized in Table III and Fig. 4. Table III and Fig. 4 also summarize the temperature dependence of the  $k_2$  value at 240–340K, and fitting this data by the Arrhenius equation yields an expression of  $k_2 = (2.43 \pm 0.52) \times 10^{-11} \exp[(-481.2 \pm 60)/T]$  for the reaction of *n*-hexane with OH over this temperature range. This is consistent with the previous Arrhenius expression of  $k_{\text{hexane}+\text{OH}} = 2.60 \times 10^{-11} \exp[(-480)/T]$  determined by DeMore and Bayes [22] at 292–367K. In addition, within the experimental uncertainty our  $k_2$  values are also in good agreement with that determined by Donahue et al. [20] at 300–340K using the absolute rate technique, as shown in Fig. 4. A comparison of the regression lines of Fig. 4 show more agreement between the current work and the recommended Arrhenius expression [2] in the lower temperature regime than at higher temperatures. Both show that the reaction (2) rate constant also has a positive temperature dependence over 240–340K. An activation energy of  $0.96 \pm 0.12 \text{ kcal mole}^{-1}$  is calculated for reaction (2), which is also in good agreement with the recommended value of  $0.80 \text{ kcal mole}^{-1}$  [1].



**Figure 4** Arrhenius plot for the reaction of *n*-hexane + OH at 240–340K along with available experimental data in literature. The dotted line generated over the temperature range of the current work using the recommended Arrhenius expression in [2]. Calculated data using the Arrhenius expression in [22] is also included for comparison.

## Atmospheric Lifetime of *n*-Hexane and *n*-Heptane

The reaction of *n*-hexane and *n*-heptane with the hydroxyl radical represent the primary means for the atmospheric removal [33] of these species. The atmospheric lifetime of these molecules is estimated using the following equation:

$$\tau_{\text{alkane}} \approx 1/(k_{\text{alkane}+\text{OH}}[\text{OH}]) \quad (\text{II})$$

where  $\tau_{\text{alkane}}$  is the atmospheric lifetime of the alkane due to OH removal,  $k_{\text{alkane}+\text{OH}}$  is the rate constant for the reaction of the alkane with OH radical at the typical tropospheric temperature of 277K, and [OH] is the atmospheric concentrations of the hydroxyl radicals. The average tropospheric hydroxyl radical concentration has been previously reported in the literature as  $(8.1 \pm 0.9) \times 10^5$  molecules  $\text{cm}^{-3}$  [34]. Using the  $k_{\text{alkane}+\text{OH}}(277\text{K})$  values determined in the present work, the atmospheric lifetime for *n*-hexane and heptanes are estimated to be 74 and 59 h, respectively.

## CONCLUSION

The kinetics of reactions of the OH radical with *n*-heptane and *n*-hexane have been investigated between 240–340K using the discharge flow system coupled to a mass spectrometer combined with the relative rate (RR/DF/MS) technique. To our best knowledge, the rate constants for the reactions at tropospheric temperatures are determined for the first time. For *n*-heptanes reaction with OH, both *n*-octane and *n*-nonane were used as reference compounds to check the accuracy and consistency of kinetic results. At 298K, rate constants of *n*-heptane with OH were determined to be  $k_{1,\text{octane}} = (6.68 \pm 0.50) \times 10^{-12}$   $\text{cm}^3$  molecule $^{-1}$  s $^{-1}$  and  $k_{1,\text{nonane}} = (6.64 \pm 1.36) \times 10^{-12}$   $\text{cm}^3$  molecule $^{-1}$  s $^{-1}$ , respectively which are in good agreement with the current literature value. The rate constant for reaction of *n*-hexane with the OH radical was determined using *n*-heptane as a reference, and at 298K the rate constant was determined to be  $(5.00 \pm 0.40) \times 10^{-12}$   $\text{cm}^3$  molecule $^{-1}$  s $^{-1}$ . The increase in the reactivity of the OH radical toward *n*-heptane versus *n*-hexane may be due to the fact that *n*-heptane has one additional -CH<sub>2</sub>-group, which provides an additional reaction site for the OH radical. The Arrhenius expression for these chemical reactions have been determined to be  $k_{1,\text{octane}} = (2.25 \pm 0.21) \times 10^{-11} \exp[(-293 \pm 37)/T]$  for reaction of *n*-heptane reaction with OH, and  $k_2 = (2.43 \pm 0.52) \times 10^{-11} \exp[(-481.2 \pm 60)/T]$  for *n*-hexane reaction with OH, respectively, which are in good agree-

ment with that reported by DeMore and Bayes [22] and Wilson et al. [23] in the overlapped temperature range of 292–340K. Finally, the atmospheric lifetime for the *n*-heptane and *n*-hexane is estimated to be 59 and 74 h based on the kinetics results of the present work.

## BIBLIOGRAPHY

1. Atkinson, R. *Chem Rev* 1985, 85, 69–201.
2. Atkinson, R. *Atmos Chem Phys* 2003, 3, 2233–2307.
3. Koffend, J. B.; Cohen, N. *Int J Chem Kinet* 1996, 28, 79–87.
4. Anderson, R. S.; Huang, L.; Iannone, R.; Thompson, A. E.; Rudolph, J. *J Phys Chem A* 2004, 108, 11537–1154.
5. Xu, X.; Williams, J.; Plass-Dulmer, C.; Berresheim, H.; Salishbury, G.; Lang, L.; Li, Z. *Atmos Chem Phys Discuss* 2003, 3, 1461–1475.
6. O'Neil, M. J.; Heckelman, P. E.; Koch, C. B.; Roman, K. J.; Kenny, C. M.; D'Arecca, M. R., Eds.; *The Merck Index: An Encyclopedia of Chemicals, Drugs, and Biologicals*; Merck and Company, Inc.: Whitehouse Station, NJ, 2006.
7. Lloyd, A. C.; Darnall, K. R.; Winer, A. M.; Pitts, J. N., Jr. *J Phys Chem* 1976, 80, 789–794.
8. Wu, C. H.; Japar, S. M.; Niki, H. *J Environ Sci Health* 1976, A11, 191–200.
9. Campbell, I. M.; McLaughlin, D. F.; Handy, B. *J Chem Phys Lett* 1976, 38, 362–364.
10. Atkinson, R.; Aschmann, S. M.; Carter, W. P. L.; Winer, A. M.; Pitts, J. N. *Int J Chem Kinet* 1982, 14, 781–788.
11. Atkinson, R.; Aschmann, S. M.; Carter, W. P. L. *Int J Chem Kinet* 1983, 15, 51–61.
12. Atkinson, R.; Carter, W. P. L.; Aschmann, S. M.; Winer, A. M.; Pitts, J. N., Jr. *Int J Chem Kinet* 1984, 16, 469–481.
13. Klein, T.; Barnes, I.; Becker, K. H.; Fink, E. H.; Zabel, F. *J Phys Chem* 1984, 88, 5020–5025.
14. Klöpffer, W.; Frank, R.; Kohl, E.-G.; Haag, F. *Chemiker-Zeitung* 1986, 110, 57–61.
15. Barnes, I.; Bastian, V.; Becker, K. H.; Fink, E. H.; Nelsen, W. *J Atmos Chem* 1986, 4, 445–466.
16. Behnke, W.; Nolting, F.; Zetzsch, C. *J Aerosol Sci* 1987, 18, 65–71.
17. Nolting, F.; Behnke, W.; Zetzsch, C. *J Atmos Chem* 1988, 6, 47–59.
18. Behnke, W.; Hollander, W.; Koch, W.; Nolting, F.; Zetzsch, C. *Atmos Environ* 1988, 22, 1113–1120.
19. McLoughlin, P.; Kane, R.; Shanahan, I. *Int J Chem Kinet* 1993, 25, 137–148.
20. Donahue, N. M.; Anderson, J. G.; Demerjian, K. L. *J Phys Chem A* 1998, 102, 3121–3126.
21. Ferrari, C.; Roche, A.; Jacob, V.; Foster, P.; Baus, P. *Int J Chem Kinet* 1996, 28, 609–614.
22. DeMore, W. B.; Bayes, K. D. *J Phys Chem A* 1999, 103, 2649–2654.

23. Wilson, E. W., Jr.; Hamilton, W. A.; Kennington, H. R.; Evans III, B.; Scott, N. W.; DeMore, W. B. *J Phys Chem A* 2006, 110, 3593–3604.
24. Li, Z. *Chem Phys Lett* 2004, 383, 592–600.
25. Li, Z.; Singh, S.; Woodward, W.; Dang, L. *J Phys Chem A* 2006, 110, 12150–12157.
26. Sander, S. P.; Friedl, R. R.; Golden, D. M.; Kurylo, M. J.; Huie, R. E.; Orkin, V. L.; Moortgat, G. K.; Ravishankara, A. R.; Kolb, C. E.; Molina, M. J.; Finlayson-Pitts, B. J. *JPLPublication 02–25*, NASA; JPL/California Institute of Technology: Pasadena, CA, 2003.
27. Arutyunov, V. S.; Buben, S. N.; Chaikin, A. M. *Kinet Catal* 1979, 20, 465.
28. Zelenov, V. V.; Kukui, A. S.; Dodonov, A. F.; Aleinikov, N. N.; Kashtanov, S. A.; Turchin, A. V. *Khim Fiz* 1991, 10, 1121–1124.
29. Baulch, D. L.; Cobos, C. J.; Cox, R. A.; Esser, C.; Frank, P.; Just, T.; Kerr, J. A.; Pilling, M. J.; Troe, J.; Walker, R. W.; Warnatz, J. *J Phys Chem Ref Data*, 1992, 21, 419–734.
30. Miyoshi, A.; Tsuchiya, K.; Yamauchi, N.; Matsui, H. *J Phys Chem* 1994, 98, 11452–11458.
31. Cohen, N.; Westberg, K. R. *J Phys Chem Ref Data* 1991, 20, 1211–1131.
32. Steinfeld, J. I.; Francisco, J. S.; Hase, W. L. *Chemical Kinetics and Dynamics*; Prentice Hall: New York, 1989.
33. Li, Z.; Jeong, G.; Hansen, J. C.; Good, D. A.; Francisco, J. S. *Chem Phys Lett* 2000, 320, 70–76.
34. Prinn, P.; Cunnold, D.; Simmonds, P.; Alyea, F.; Bold, R.; Crawford, A.; Fraser, P.; Gutzler, D.; Hartley, D.; Rosen, R.; Rasmussen, R. *J Geophys Res* 1992, 97, 2445–2461.
35. Zellner, R.; Erler, K.; Field, D. *Symp Int Combustion Proc* 1977, 16, 939.
36. Nicholas, J. E.; Vaghijiani, G. L. *J Chem Phys* 1989, 91, 5121–5123.

Copyright of International Journal of Chemical Kinetics is the property of John Wiley & Sons, Inc. and its content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.