# Rate coefficients for the reactions of OH radical with C3-C11 alkanes determined by the relative rate technique

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**Abstract**: Rate coefficients for the reactions of OH radicals with C3-C11 alkanes were determined using the multivariate relative rate technique. A total of 25 relative rate coefficients at room temperature and 24 Arrhenius expressions–in different temperature range were obtained. Notably, a new room temperature relative rate constant for 3-methylheptane that had not been previously reported was determined, and the obtained $k_{OH}$ values (in units of $10^{-12}$ $cm^3$ molecule$^{-1}$ s$^{-1}$) was 7.71±0.35. Interestingly, whilst results for n-alkanes agreed well with available structure activity relationship (SAR) calculations, the three cyclo-alkanes and one trimethylpentane were found to be less reactive than predicted by SAR. Conversely, the SAR estimate for 2,3-dimethylbutane were approximately 25% lower than the experimental value, highlighting that the limited understanding of the oxidation chemistry of these compounds. Arrhenius expressions (in units of $cm^3$ molecule$^{-1}$ s$^{-1}$) for the reactions of various branched alkanes with OH radical were determined for the first time: 2-methylheptane, $(1.62\pm0.37)\times10^{-11}$ exp $[-(265\pm70)/T]$, and 3-methylheptane, $(3.54\pm0.45)\times10^{-11}$ exp $[-(374\pm49)/T]$. The reactivity relation of saturated alkanes with OH radicals and chlorine atoms was obtained: $\log_{10}[k_{(Cl+alkanes)}] = 0.569\times\log_{10}[k_{(OH+alkanes)}]-3.111$ ($R^2$ =0.86). In addition, the rate coefficients for the 24 previous studied OH + alkanes reactions were consistent with existing literature values, demonstrating the reliability and efficiency of this method for simultaneous investigation of gas-phase reaction kinetics.

**Keywords:** Relative rate coefficients; Atmospheric simulation chamber; Alkanes; OH radical; Arrhenius expressions

# 1. Introduction

Volatile organic compounds (VOCs), a category of compounds found ubiquitously in the atmosphere, primarily consist of alkanes, alkenes, aromatics and oxygenated volatile organic compounds (OVOCs) (Lewis et al., 2000; Goldstein and Galbally, 2007; Anderson et al., 2004). Research has shown that alkanes, including straight-chain, branched-chain, and cyclic alkanes within the C3-C11 range, often constitute a significant portion to VOCs (Liang et al., 2023; Dunmore et al., 2015), and they could be emitted into the atmospheric environment through natural and anthropogenic sources, e.g., C5-alkanes emitted from gasoline usage and C6-alkanes and higher homologous VOCs emitted as a consequence of their usage as solvents and from fuel evaporation. (Atkinson, 2000; Guenther, 2002; Atkinson and Arey, 2003). In the troposphere, alkanes are degraded and removed from the atmosphere via gas-phase oxidation reactions with OH and $NO_3$ radicals, Cl atoms and ozone ($O_3$) (Atkinson and Arey, 2003; Shi et al., 2019; Finlayson-Pitts and Pitts, 1997; Atkinson, 2000). These oxidation processes will form a photochemical smog in the presence of NOx and light, causing regional photochemical pollution (Fiore et al., 2005; Ling and Guo, 2014). Additionally, some secondary oxides produced by the oxidation of alkanes can form secondary organic aerosol (SOA) through homogeneous nucleation or condensation onto existing primary particles (Sun et al., 2016). To fully understand the role of alkanes in atmospheric chemistry, accurate chemical reaction rate data is an important criterion for evaluating its reactivity (Shaw et al., 2018).

Numerous laboratories have conducted research on the kinetics of the reaction between alkanes and OH radicals using the absolute rate constant method and the relative rate constant method. The absolute rate constant method (such as flash photolysis and emission flow) involves calculating the reaction kinetics parameter $k_{OH}$ for organic compounds with OH radicals during the experimental process by directly measuring changes in OH radical concentration or the concentration of the target compound. Greiner measured the first kinetic data for the reaction of OH radicals with three alkanes in the Ar system at 300 K using the flash photolysis-resonance fluorescence technique (Greiner, 1967). Over the next decade, Gorse et al., Overend et al. and Darnall et al. obtained kinetic data for the reaction of OH radicals with selected alkanes in the carbon monoxide, He and $N_2$ system, respectively (Gorse and Volman, 1974; Overend et al., 1975; Darnall et al., 1978). Unlike the absolute rate constant method, the relative rate method relied on the known rate constant for the reaction of a reference compound with OH radicals, with the reference reaction rate coefficient needing to be similar to that of the compound under study to enhance measurement sensitivity. By monitoring the simultaneous decay of the target and reference

compounds in the presence of OH radicals due to competitive response mechanisms, the rate constant for the reaction of OH radicals with the target compound can be determined (Atkinson and Arey, 2003; Shaw et al., 2018). From 1980s to 2020s, dozens of papers for the rate coefficients of alkanes with OH radical measured by relative rate mehod have been published. For example, Shaw et al. and Phan and Li obtained rate constants of a series of alkanes in the $N_2$/He system (Phan and Li, 2017; Shaw et al., 2018; Shaw et al., 2020). Anderson et al. obtained the $k_{OH}$ of C2-C8 several n-alkanes and cyclic alkanes by the relative technique in the air system at 296 ± 4 K (Anderson et al., 2004). However, the majority of experiments were conducted solely on C2-C6 alkanes, more complex and multifunctional alkanes are often poorly constrained or unmeasured.

Temperature has an important influence on the reaction rate constants of alkanes and OH radicals. The reaction rate constants of several n-alkanes with OH radicals measured by Greiner increased by about 70% in the range of 300-500 K (Greiner, 1970a). Perry et al's research found that the rate constants of n-butane multiplied by 72% as the temperature rose from 297 K to 420 K (Perry et al., 1976). And the rate coefficients of 10 n-alkanes and cycloalkanes obtained by Donahue et al. also increased in varying degrees at 300-390 K (Donahue et al., 1998). However, most reported experimental studies on the reactivity of OH radicals with a series of alkanes focus on temperatures ≥290 K (Greiner, 1970a; Perry et al., 1976; Finlaysonpitts et al., 1993; Donahue et al., 1998; Atkinson, 2003; Badra and Farooq, 2015), with relatively few studies at low temperatures (Demore and Bayes, 1999; Li et al., 2006; Wilson et al., 2006; Sprengnether et al., 2009; Crawford et al., 2011). In addition, a further alkane had only two, or fewer, individual OH radical rate coefficient measurements available in the mentioned temperature range, e.g., 3-methylheptane, and it is unclear whether the rate constants for the reactions of OH radicals with alkanes differ in a mixed system containing oxygen compared to an inert gas system. Therefore, further investigations are required to explore the variations in the rate constants for different types of alkanes at various temperatures.

In this study, the rate constants for the reactions of 25 different C3-C11 alkanes with OH radicals were determined using the multivariate relative rate method, including linear alkanes, cycloalkanes, and methyl-alkanes. To validate the rate constants for the reaction between alkanes and OH radicals, multiple comparisons were made with previous literature and structure–activity relationship (SAR) estimated values. Additionally, the rate constants of certain straight-chain, branched-chain, and methyl-cycloalkanes were measured at 273-323 K.

## 2. Methods

### 2.1 Experiment

2.1.1 Atmospheric simulation chamber

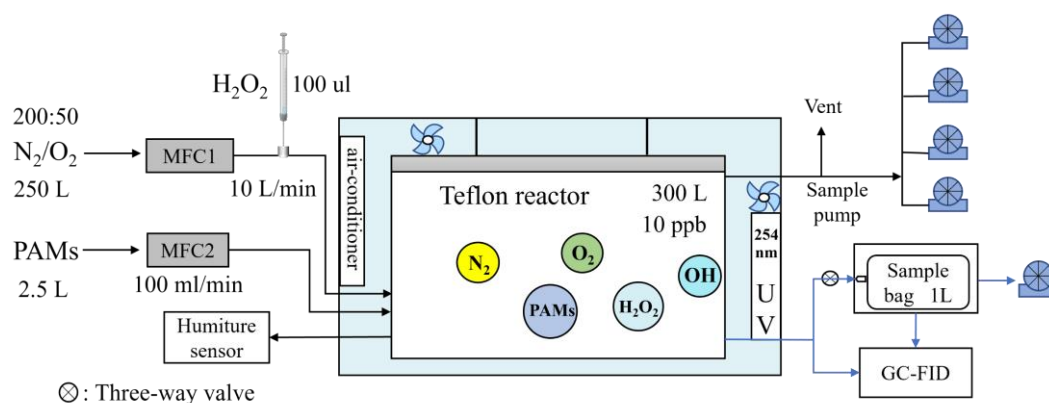



Figure 1. A schematic of the experimental device

As shown in Fig. 1, the chamber experiments were performed at atmospheric pressure in a climate-controlled box with a temperature range of 263-333 K (accuracy of $\pm$ 0.1 K). A 300 L Teflon airbag was suspended in the climate-controlled box to serve as the reaction system. The box was equipped with two Teflon-coated fans for rapid chemical mixing and a 254 nm ultraviolet lamp for photolysis of hydrogen peroxide ($H_2O_2$) to produce OH radicals. The inner walls of climate-controlled box were constructed with reflective steel plates to enhance ultraviolet light utilization. Bath gas ($N_2$ or $O_2$) and NMHCs were introduced into the Teflon bag through mass flow controllers with flow rate of 25 L min$^{-1}$ and 100 mL min$^{-1}$, respectively, while excess $H_2O_2$ respect to VOCs was injected through a three-way valve using a micro syringe. Initial conditions of the different species introduced into the reactor for each experiment are outlined in Table S1 in the Supplementary Material. By varying the presence of $H_2O_2$, turning on/off the light, a series of observations were generated, such as $N_2$ + NMHCs + dark reaction, $N_2$ + NMHCs + hv (254 nm), and $N_2$ + NMHCs + $H_2O_2$ + dark reaction.

2.1.2 Gas sampling and analysis

NMHCs Analyzer (GC-FID) with a time resolution of 1 hour independently developed by the Research Center for Eco-Environmental Sciences (RCEES) was used to analyze 25 C3-C11 alkanes. The sample gas was enriched by a 60-80 mesh Carbopack B adsorption tube under the condition of 183.15 K, and then the adsorption tube was rapidly heated to 453.15 K. The 25 alkanes were detected by FID at

110      523.15 K after programmed heating at 253.15 K, 303.15 K and 433.15 K in 30 min (Liu et al., 2016).

111      Figure S1(a) reveals that the mixed gas diluted with $N_2$ underwent a 14-hour reaction in a Teflon reactor

112 without light. The $K_d$ values ranged from 1.3 to 4.8 (the units are $\times 10^{-4}$ ppbv/h), implying negligible

113 influence from factors such as alkane loss from reactor walls, self-consumption, or airbag leakage. Figure

114 S1(b) illustrates that the peak height variation for 25 alkanes + 50 μl of $H_2O_2$ within 15 hours was less

115 than 3%, indicating the insignificance of dark reactions between $H_2O_2$ and alkanes. When the same

116 concentration mixed gas was irradiated for 7 hours without $H_2O_2$, alkane concentration changes were

117 depicted in Fig. S2. The results indicated that minimal impact from alkane photolysis on OH radical

118 reaction rate constant determination.

119      To obtain the reaction rate constants of alkanes with OH radicals in 1-2 hour, the alkanes mixture

120 exiting the reactor was collected in more than ten polyvinyl fluoride (PVF) sampling bag (1.0 L) using a

121 transparent vacuum sampling device for GC-FID. Prior to use, the empty sampling bag was flushed with

122 high-purity nitrogen 3 times and placed within the vacuum sampler - a system utilizing an oil-free

123 diaphragm air pump to create a vacuum. The initial concentrations of alkanes sample were collected

124 before the lamp on, and the following sampling process occurred every 10 minutes. Collected samples

125 were subsequently analyzed using a self-developed automated injection system for PVF bag.

126 2.1.3 Relative rate technique

127      The rate coefficients were measured by the relative rate method (Atkinson, 1986). The basic principle

128 is that the rate constant for the reaction of the reactant used as a reference with OH radicals is known, rate

129 constant for the reaction of OH radicals with the target compound can be determined by monitoring the

130 simultaneous decay of the target and reference compounds in the presence of OH radicals due to the

131 competitive response mechanism. Additionally, an important criterion for the selection of reference

132 compounds, that is, the reference rate coefficient needs to be similar to the one under study in order to

133 improve sensitivity. To ensure that the reactants only react with OH radicals, the OH radicals need to be

134 in excess in the experiment. The research method of this work is based on the multivariate relative rate

135 method published by Shaw et al. (Shaw et al., 2018), taking the mixed system as the research object,

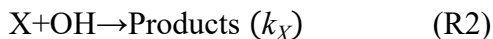
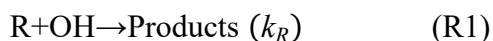
136 broadening the range of compounds that can be examined.

137      Taking R (reference compounds) and X (target compounds) as examples, the reaction of OH radicals

138 can be described as follows:

$$139 \quad \text{R+OH} \rightarrow \text{Products } (k_R) \qquad \text{(R1)}$$

$$140 \quad \text{X+OH} \rightarrow \text{Products } (k_X) \qquad \text{(R2)}$$

$$141 \quad -\frac{d[R]}{dt} = k_R[\text{OH}][R] \qquad \text{(R3)}$$

$$142 \quad -\frac{d[X]}{dt} = k_X[\text{OH}][X] \qquad \text{(R4)}$$

$$143 \quad \ln\left(\frac{[R]_0}{[R]_t}\right) = k_R \cdot \int [\text{OH}]dt \qquad \text{(R5)}$$

$$144 \quad \ln\left(\frac{[X]_0}{[X]_t}\right) = k_X \cdot \int [\text{OH}]dt \qquad \text{(R6)}$$

$$145 \quad \ln\left(\frac{[X]_0}{[X]_t}\right) = \frac{k_X}{k_R} \cdot \ln\left(\frac{[R]_0}{[R]_t}\right) \qquad \text{(R7)}$$

146    Where $[R]_0$ and $[X]_0$ are the concentrations of reference compounds and target compounds before

147    turning on the light; $[R]_t$ and $[X]_t$ are the corresponding concentrations after turning on the light for time

148    t. $k_R$ and $k_X$ refer to the second-order rate constants for the reaction of the reference compounds and target

149    compounds with OH radicals.

150    2.1.4 Choice of reference $k$ values

151    It is critical to choose appropriate reference compounds in a kinetics study using the relative rate

152    technique. Some reported values of the rate constants for reactions of C3-C11 alkanes with OH radicals

153    have been measured by different methods in different laboratories, and these measurement results may be

154    quite different. When these rate constants are measured by the relative rate technique, choosing different

155    reference values will lead to a change of the final experimental target rate constants. In this work, selecting

156    3 different commonly used reference compounds (n-Hexane, Cyclohexane, n-Octane) to determine the

157    rate constants for each reaction at room temperature to check the consistency of kinetic results. The

158    selection of $k$ values for reference compounds and the literature data assessment and comparison gives

159    priority to the available expert-evaluated rate constants wherever possible. Here we used the

160    recommended expert-evaluated data of database for Version 2.1.0 of McGillen et al. (Database for the

161    Kinetics of the Gas-Phase Atmospheric Reactions of Organic Compounds – Eurochamp Data Center),

162    which is relatively comprehensive and provides rigorously evaluated rate coefficients for many species.

163    Among them, at $298 \pm 1$ K, the $k$ values (in units of $cm^3$ molecule$^{-1}$ s$^{-1}$) of the three reference compounds

164    selected respectively are expert-evaluated rate constants: $k_{OH+n\text{-}Hexane}=4.97\times10^{-12}$, $k_{OH+Cyclohexane}=6.69\times10^{-}$

[12], $k_{OH+n\text{-}Octane}=8.48\times10^{-12}$, which is fitted or manually entered data from multiple sources. However, the value of the reference compound at different temperatures (273-323 K) is different than the room temperature. A detailed explanation is reflected in Sec. 3.3.

### 2.1.5 Materials

The air bath gas was obtained by a mix of nitrogen (200 L) and oxygen (50L). $H_2O_2$ (30%) was provided by Sinopharm Chemical Reagent Co., Ltd. The standard gas (PAMs) is a mixed standard sample of 57 kinds of NMHCs produced by Linde Spectra Environmental Gases (Alpha, NJ). Sampling bag (PVF, 1 L) was provided by Dalian Delin Gas Packing Co., Ltd. The pump is the NMP830 KNDC model produced by KNF, Germany, with a maximum air sampling rate of 23 L/min. The climate-controlled box (ZRG-1000D-C0203) is provided by Shanghai Proline Electronic Technology Co., Ltd.

## 2.2 Estimation of the rate constant at 298 K (SAR)

In the past few decades, researchers have been devoted to finding a reasonable theoretical estimation method for the kinetic rate constants (Cohen, 1991). Structure-Activity Relationship (SAR) established and developed by Kwok and Atkinson et al. (Kwok and Atkinson, 1995), is the most widely used estimation method of rate constants. Based on the relationship between the structure and the reaction activity of the compounds, this method assumes that the hydrogen extraction reaction mainly occurs in the saturated compounds and the addition reaction mainly occurs in the unsaturated compounds, which is used to estimate the gaseous rate constants for the reactions of most VOCs with OH radicals. An advantage of the rate constant estimation is that it gives a measure of the rates of attack at different sites in the molecule, which is then useful in predicting the overall temperature dependence. The rate constant estimated by SAR method is in good agreement with the experimental data. In this relationship, the calculation of the rate constant of the hydrogen atom on the C-H bond is based on the evaluation of the rate constant of the $-CH_3$, $-CH_2-$, $>CH-$ group. The relationship between the group structure and the rate constant is as follows:

$$K(CH_3\text{-}X)=K_{prim}^0 F(X)$$

$$K(X\text{-}CH_2\text{-}Y)=K_{sec}^0 F(X)F(Y)$$

$$K(X\text{-}CH(Y)Z)=K_{tert}^0 F(X)F(Y)F(Z)$$

$$K_{tot} = \sum [K(CH_3\text{-}X) + K(X\text{-}CH_2\text{-}Y) + K(X\text{-}CH(Y)Z)]$$

192

193 Where, $K_{tot}$ represents the rate constant of each target compound. $K_{prim}^0$, $K_{sec}^0$, $K_{tert}^0$ represent the

194 rate constants of each -$CH_3$, -$CH_2$- and >CH-. For standard substituent groups such as -$CH_3$, F(-

195 $CH_3$)=1.00, X, Y and Z represent substituent groups, F(X), F(Y) and F(Z) refer to the activity coefficient

196 of substituents (X, Y, Z) at different positions on carbon groups. At room temperature, F(-$CH_2$-)=1.23,

197 F(>CH-)=1.23. Based on an extensive review of kinetic literature values for linear alkanes at room

198 temperature, Atkinson and Kwok et al derived the values of $K_{prim}^0$, $K_{sec}^0$, $K_{tert}^0$ at room temperature,

199 $K_{prim}^0$=0.136×$10^{-12}$, $K_{sec}^0$=0.934×$10^{-12}$, $K_{tert}^0$=1.94×$10^{-12}$, the unit is $cm^3$ molecule$^{-1}$ s$^{-1}$. After that, many

200 researchers continued to updated and modified some parameters based on the method of Atkinson and

201 Kwok (Kwok and Atkinson, 1995), and obtained the new fundamental rate constants for different

202 positional groups, some examples include: Neeb, Wilson et al., and Jenkin et al. (Neeb, 2000; Wilson et

203 al., 2006; Jenkin et al., 2018).

## 3. Result and Discussion

204

### 3.1 Results from relative rate experiments at 298 K

205

206 The rate constants for the reactions involving OH radical with C3-C11 alkanes in the mixed system

207 were determined at 298±1 K. The concentration curves of target alkanes and the reference compound (n-

208 Hexane) were plotted in Fig. 2. As shown in Fig. 2, the decay of both target and reference compounds

209 correlated well with eq. (7), and high correlation coefficients ($R^2$) were observed for most alkanes,

210 exceeding 0.99. Table 1 and Table S2 listed the obtained $k_{OH}$ for C3-C11 alkanes under three bath gases

211 using the related reference compounds. The error bars (1σ) in Table 1 accounted for reference rate constant

212 uncertainty, and experimental parameter uncertainties (pressure, temperature, flow rate, reactant

213 concentration). The results indicated strong agreement (within <15%) between rate constants for 25 C3-

214 C11 straight-chain, branched-chain, and cycloalkanes, using different reference compounds. For example,

215 the $k_{OH}$ obtained for propane with n-hexane, cyclohexane and n-octane as the reference compound were

216 (1.38±0.01)×$10^{-12}$, (1.25±0.03)×$10^{-12}$ and (1.34±0.04)×$10^{-12}$ (the units are $cm^3$ molecule$^{-1}$ s$^{-1}$),

217 respectively (within 10%). This suggests that reference compound variation minimally affects results,

218 indicating reliable experimental methods and data. Notably, the rate constant for 3-Methylheptane's

reaction with OH radicals at room temperature was determined for the first time. As shown in Fig. 3, for the different bath gases, the obtained $k_{OH}$ for C3-C11 alkanes showed high agreement. Meanwhile, it can also be observed from the figure that most of the rate coefficients obtained are very similar to the expert-evaluated values of the database by the McGillen et al. However, 2,4-Dimethylpentane is an exception, the $k_{OH}$ value obtained in this study is about 20% lower than the recommended value, but it is similar to expert-evaluated value by Atkinson and Arey (Atkinson and Arey, 2003). Additionally, it can be clearly seen in the figure that the reactivity of linear alkanes ($RCH_2R$) with OH radicals increasing as the number of carbon atoms in the hydrocarbon molecules increases, indicating that the increase of R-terminal alkyl chain length will provide additional hydrogen extraction sites. For each additional $CH_2$ group from C3-C11, the reaction rate constant increases about 0.95-1.81 (the unit is $10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$), reflects the fact that the main way is to extract the H atom from the second-order C-H bond. For branching alkanes, for example, 2,2-Dimethylbutane and 2,3-Dimethylbutane, it is obvious that the addition of CH group increases the reaction rate constants with OH radical to a great extent. For cyclic alkanes, such as cyclopentane, methylcyclopentane, cyclohexane and methylcyclohexane, it can also be seen that the reactivity increase with the increase of cycle size. By comparing the reaction rate constant of cyclopentane and cyclohexane (methylcyclopentane and methylcyclohexane), it is found that for cyclic alkanes, each $CH_2$ group reaction rate increases by about $2.37×10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. It can be seen from the reaction rate constant of cyclopentane and methylcyclopentane (cyclohexane and methylcyclohexane) that the reaction rate constant increases about $2.06×10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for cycloalkanes with each increase of methyl.

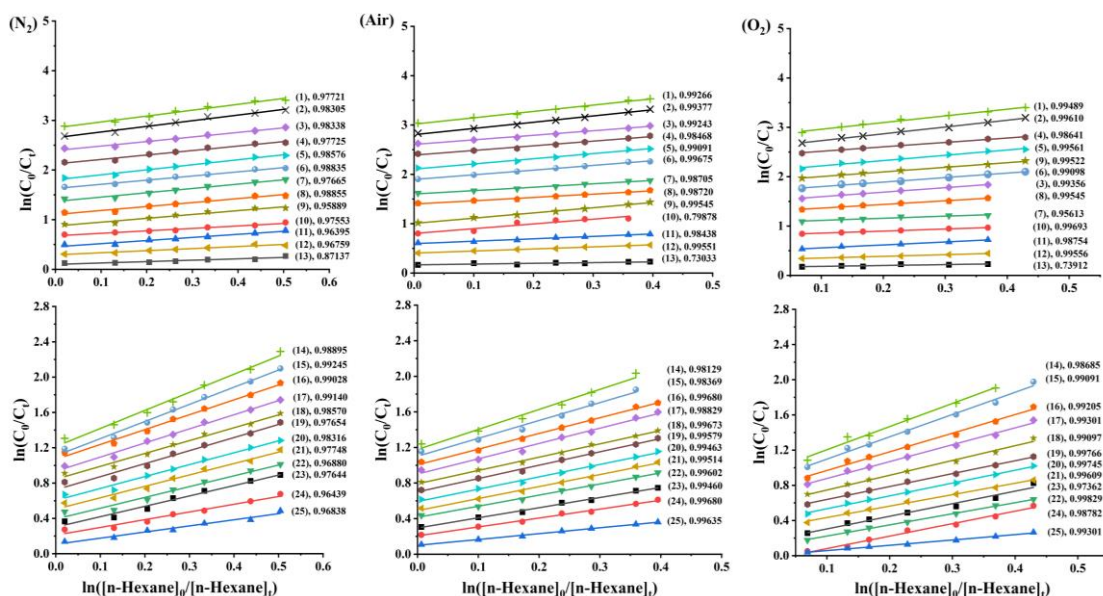



Figure 2. Typical kinetic data as acquired with the multivariate relative rate technique at 298 K and a fixed reaction time of 70 min for the reaction of C3-C11 alkanes with the OH radical using n-hexane as reference compound in different bath gases ($N_2$, Air, $O_2$). The numbers in parentheses correspond to each substance, followed by the correlation coefficient $R^2$. The following data have been displaced for reasons of clarity: ($N_2$): (1) Methylcyclopentane, (2) Cyclohexane, (3) Cyclopentane, (4) 2-Methylpentane, (5) 2,3-Dimethylbutane, (6) 2,4-Dimethylpentane, (7) Isopentane, (8) 1-pentane, (9) 3-Methylpentane, (10) Isobutane, (11) n-Butane, (12) 2,2-Dimethylbutane, (13) Propane (14) n-Undecane, (15) n-Decane, (16) Nonane, (17) Methylcyclohexane, (18) n-Octane, (19) 3-Methylheptane, (20) 2-Methylheptane, (21) 2,3,4-Trimethylpentane, (22) 1-Heptane, (23) 2-Methylhexane, (24) 3-Methylhexane, (25) 2,2,4-Trimethylpentane vertically displaced by 2.8, 2.6, 2.4, 2.1, 1.8, 1.6, 1.4, 1.1, 0.9, 0.7, 0.5, 0.3, 0.1, 1.2, 1.1, 1, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.25, 0.1 units, respectively; (Air) Each alkane (in the above order) vertically displaced by 3, 2.8, 2.6, 2.4, 2.1, 1.9, 1.6, 1.4, 1, 0.8, 0.6, 0.4, 0.1, 1.2, 1.1, 1, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, 0.1 units, respectively; ($O_2$) Each alkane (in the above order) vertically displaced by 2,8, 2.6, 1.5, 2.4, 2,1, 1.7, 1, 1.3, 1.9, 0.8, 0.5, 0.3, 0.1, 1, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.1 units, respectively (Not mentioned defaults to 0).

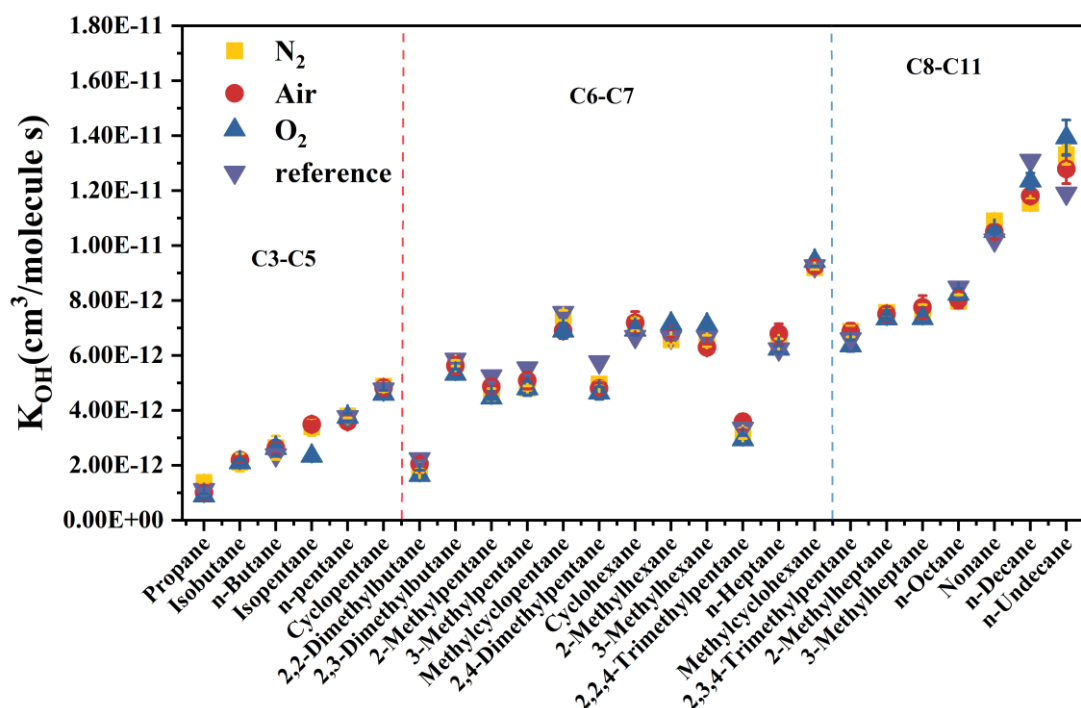



Figure 3. Comparison of rate constants of C3-C11 alkanes in different bath gases ($N_2$, Air, $O_2$) with expert-evaluated data at 298±1 K. The error bar was taken as 1σ.

The obtained $k_{OH}$ values for C3-C11 alkanes were compared with literature-reported values (Table

1). For several n-alkanes, such as n-butane, the average rate constants obtainedin the air gas is (2.63±0.23), the unit is $10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (applicable to all units involved in this paragraph). The result is highly consistent with the value (2.72±0.27) obtained by Perry et al using flash photolysis resonance fluorescence technique and the values (2.56±0.25) obtained by Greiner (Greiner, 1970a), with a consistency of 3% or better (Perry et al., 1976). Although slightly higher by 7% compared to Talukdar et al. (Talukdar et al., 1994) using absolute techniques (2.46±0.15), when considering the errors, they still exhibit consistency within a certain range. Compared to the value obtained by DeMore et al. (Demore and Bayes, 1999) using the relative rate method (2.36±0.25) and the expert-evaluated data (2.36) of McGillen et al.'s database, these values are higher by 11%.

**n-pentane (n-Heptane).** As in the n-butane case, the derived rate constants for n-pentane and n-heptane are in excellent agreement (4% or better at 298 K) with previous studies (Donahue et al., 1998; Atkinson, 2003; Atkinson and Arey, 2003; Wilson et al., 2006; Crawford et al., 2011; Calvert et al., 2015; Morin et al., 2015).

**n-Octane (Nonane).** The reaction rate constants of n-Octane and OH radicals are in extremely good agreement with the values reported in the literature (within 5%) (Greiner, 1970a). Same for Nonane, consistency with previous studies is less than 8% (Greiner, 1970a; Atkinson et al., 1982; Ferrari et al., 1996; Atkinson and Arey, 2003; Li et al., 2006).

**n-Decane.** The obtained average $k_{OH}$ for n-decane in the air system was (1.18±0.02), the unit is $10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.When considering experimental error, these results are consistent with the relative value (1.29±0.10) obtained by Li et al. (Li et al., 2006) and the reviewed value (1.10) of Atkinson and Arey (Atkinson and Arey, 2003), with about a consistency of 6%-9%.

**n-Undecane.** The obtained average $k_{OH}$ for n-decane in the air system was (1.33±0.16), the unit is $10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. It is about 8% higher than the previous research (Atkinson and Arey, 2003; Sivaramakrishnan and Michael, 2009; Calvert et al., 2015).

For the cycloalkanes, like cyclopentane, the average rate constants are 4.88±0.19, 4.82±0.27, 4.59±0.14, respectively, the unit is $10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The results are in excellent agreement (8% or better) with the reviewed value (4.97) of Atkinson and Arey (Atkinson and Arey, 2003) and the relative values (4.83, 4.84) of DeMore et al. (Demore and Bayes, 1999) and Singh et al. (Singh et al., 2013) and the absolute value (5.02) of Droege et al. (Droege and Tully, 1987). And the obtained $k_{OH}$ values for cyclohexane are highly consistent (3% or better) with the absolute values ($7.14 \times 10^{-12}$, $7.19 \times 10^{-12}$)

obtained by Droege and Tully and Sprengnether et al. (Droege and Tully, 1987; Sprengnether et al., 2009).
However, this result is slightly higher than the relative value by about 5%-16%. Like the relative values
measured by DeMore and Bayes (Demore and Bayes, 1999) or Wilson et al. (Wilson et al., 2006) were
$6.70\times10^{-12}$ and $6.38\times10^{-12}$, respectively. It worth noting that the $k_{OH}$ value for methylcyclopentane in this
work is highly consistent (within 3% to 5%) with the absolute data reported by Sprengnether et al.
(Sprengnether et al., 2009). However, it is lower by approximately 15% to 18% compared to the relative
data obtained by Anderson et al. (Andersen et al., 2003). The $k_{OH}$ values for methylcyclohexane are
excellent agreement (3% or better) with other values reported by Atkinson and Arey (Atkinson and Arey,
2003) and Calvert et al. (Calvert et al., 2015).

Furthermore, for several less studied branched alkanes, such as 2-Methylhexane, 3-Methylhexane,
and 2-Methylheptane, there is only one study reported so far. Sprengnether et al. (Sprengnether et al.,
2009) conducted a study on 2-Methylhexane and 3-Methylhexane and obtained $k_{OH}$ values at room
temperature for the first time, which were $6.69\times10^{-12}$ and $6.30\times10^{-12}$ (the unit is $cm^3$ $molecule^{-1}$ $s^{-1}$),
respectively. The rate constants of 2-Methylhexane and 3-Methylhexane obtained in this work are
$(6.80\pm0.13)\times10^{-12}$ and $(6.29\pm0.11)\times10^{-12}$, respectively,which are consistent with the values obtained by
Sprengnether et al. (Sprengnether et al., 2009). However, the data for 2-Methylheptane in this work is
lower by about 17% compared to the value reported by Shaw et al. (Shaw et al., 2018).

Table 1. Comparison of Experimental in this work with the reported in the literature at 298±1 K.

| Alkanes | Reference | This work | | | Reference |
| | | $k_{OH}/k_{reference}$ ±1σ | $k_{OH}$ ±1σ (×10$^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) | $k_{OH-av}$[a] ±1σ (×10$^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) | $k_{OH}$ (×10$^{-12}$cm$^3$ molecule$^{-1}$ s$^{-1}$) |
| --- | --- | --- | --- | --- | --- |
| Propane | n-Hexane | 0.190±0.033 | (9.43±1.66) | (1.01±0.26) | 1.11[bcd] 1.09[e] 1.91[f] (1.15±0.15)[g] |
| | Cyclohexane | 0.153±0.028 | (1.03±0.18) | | |
| | n-Octane | 0.136±0.031 | (1.16±0.26) | | |
| Isobutane | n-Hexane | 0.444±0.012 | (2.21±0.06) | (2.19±0.13) | 2.12[h] 2.22[i] (2.34±0.33)[j] |
| | Cyclohexane | 0.315±0.008 | (2.08±0.02) | | |
| | n-Octane | 0.264±0.005 | (2.24±0.04) | | |
| n-Butane | n-Hexane | 0.516±0.025 | (2.56±0.12) | (2.63±0.23) | (2.36±0.25)[b] (2.72±0.27)[k] (2.56±0.25)[m] (2.46±0.15)[d] |
| | Cyclohexane | 0.398±0.017 | (2.66±0.12) | | |
| | n-Octane | 0.345±0.042 | (2.93±0.36) | | |
| Isopentane | n-Hexane | 0.684±0.033 | (3.40±0.17) | (3.49±0.25) | 3.60[e] 3.65[h] 3.50[f] |
| | Cyclohexane | 0.512±0.026 | (3.43±0.18) | | |
| | n-Octane | 0.442±0.025 | (3.75±0.22) | | |
| n-pentane | n-Hexane | 0.709±0.042 | (3.52±0.21) | (3.59±0.25) | 3.80[e] 3.98[n] 4.03[o] (3.97±0.20)[p] (4.20±0.15)[g] |
| | Cyclohexane | 0.527±0.021 | (3.53±0.14) | | |
| | n-Octane | 0.454±0.029 | (3.85±0.24) | | |
| Cyclopentane | n-Hexane | 0.951±0.033 | (4.72±0.17) | (4.82±0.27) | 4.97[e] 4.83[b] 5.02[q] (4.90±0.20)[p] 4.84[br] |
| | Cyclohexane | 0.711±0.043 | (4.76±0.29) | | |
| | n-Octane | 0.600±0.029 | (5.09±0.24) | | |
| 2,2-Dimethylbutane | n-Hexane | 0.409±0.019 | (2.03±0.09) | (2.05±0.23) | (2.23±0.15)[p] 2.15[s] 2.32[o] |
| | Cyclohexane | 0.301±0.030 | (2.02±0.20) | | |
| | n-Octane | 0.264±0.031 | (2.24±0.26) | | |

| | Solvent | | | | |
|---|---|---|---|---|---|
| 2,3-Dimethylbutane | n-Hexane | 1.095±0.061 | (5.44±0.31) | | 5.78 [e] |
| | Cyclohexane | 0.809±0.039 | (5.42±0.26) | (5.62±0.31) | (6.14±0.25) [p] |
| | n-Octane | 0.728±0.050 | (6.05±0.29) | | 6.03 [h] |
| 2-Methylpentane | n-Hexane | 0.972±0.022 | (4.83±0.11) | | 5.2 [e] |
| | Cyclohexane | 0.722±0.054 | (4.83±0.36) | (4.86±0.26) | (5.25±0.25) [p] |
| | | | | | 5.00 [f] |
| | n-Octane | 0.625±0.045 | (5.30±0.38) | | 4.75 [s] |
| 3-Methylpentane | n-Hexane | 1.014±0.030 | (5.04±0.15) | | 5.20 [e] |
| | Cyclohexane | 0.777±0.059 | (5.20±0.40) | (5.08±0.31) | (5.54±0.25) [p] |
| | | | | | 4.93 [s] |
| | n-Octane | 0.669±0.082 | (5.67±0.70) | | |
| methylcyclopentane | n-Hexane | 1.432±0.053 | (7.12±0.27) | | (7.65±0.10) [u] |
| | Cyclohexane | 1.007±0.023 | (6.73±0.15) | (7.31±0.29) | (8.60±0.30) [p] |
| | n-Octane | 0.849±0.017 | (7.00±0.24) | | (8.60±2.20) [t] |
| 2,4-Dimethylpentane | n-Hexane | 0.962±0.012 | (4.78±0.06) | | 4.80 [e] |
| | Cyclohexane | 0.721±0.046 | (4.83±0.31) | (4.80±0.20) | 5.51 [s] |
| | n-Octane | 0.596±0.026 | (5.05±0.22) | | (5.76±0.40) [p] |
| Cyclohexane | | | | | 6.97 [e] |
| | | | | | 7.14 [q] |
| | n-Hexane | 1.372±0.054 | (6.82±0.27) | | 6.38 [h] |
| | Cyclohexane | -- | -- | (7.20±0.33) | 6.70 [b] |
| | n-Octane | 0.872±0.022 | (7.39±0.19) | | (7.19±0.10) [u] |
| | | | | | (6.85±0.20) [p] |
| 2-Methylhexane | n-Hexane | 1.369±0.004 | (6.80±0.02) | | |
| | Cyclohexane | 0.993±0.022 | (6.64±0.15) | (6.80±0.13) | (6.69±0.10) [u] |
| | n-Octane | 0.800±0.031 | (6.78±0.26) | | |
| 3-Methylhexane | n-Hexane | 1.266±0.003 | (6.29±0.02) | | |
| | Cyclohexane | 0.984±0.046 | (6.58±0.31) | (6.29±0.11) | (6.30±0.10) [u] |
| | n-Octane | 0.807±0.122 | (6.73±0.74) | | |
| 2,2,4-Trimethylpentane | | | | | 3.34 [e] |
| | n-Hexane | 0.702±0.033 | (3.49±0.16) | | 3.64 [s] |
| | Cyclohexane | 0.557±0.032 | (3.72±0.21) | (3.58±0.28) | (3.34±0.25) [p] |
| | n-Octane | 0.435±0.065 | (3.69±0.55) | | (3.71±0.10) [v] |
| n-Heptane | | | | | 6.76 [e] |
| | n-Hexane | 1.280±0.066 | (6.36±0.33) | | 6.68 [y] |
| | Cyclohexane | 0.961±0.020 | (6.43±0.26) | (6.78±0.36) | 6.80 [h] |
| | n-Octane | 0.828±0.029 | (7.03±0.25) | | (6.70±0.15) [g] |
| Methylcyclohexane | n-Hexane | 1.906±0.098 | (9.48±0.49) | | 9.60 [e] |
| | Cyclohexane | 1.349±0.012 | (9.02±0.08) | (9.25±0.22) | (9.64±0.30) [p] |

| Compound | Reference | k | | Weighted average[a] | Literature |
|---|---|---|---|---|---|
| | n-Octane | 1.160±0.016 | (9.83±0.14) | | (11.8±1.00)[F] |
| | | | | | (9.50±0.14)[D] |
| | | | | | (9.29±0.10)[u] |
| 2,3,4-Trimethylpentane | n-Hexane | 1.355±0.050 | (6.73±0.25) | | 6.60[e] |
| | Cyclohexane | 1.008±0.039 | (6.74±0.26) | (6.87±0.30) | 6.50[h] |
| | n-Octane | 0.861±0.039 | (7.30±0.33) | | (6.60±0.26)[p] |
| 2-Methylheptane | n-Hexane | 1.532±0.062 | (7.62±0.31) | | |
| | Cyclohexane | 1.061±0.029 | (7.09±0.19) | (7.49±0.27) | 9.10[L] |
| | n-Octane | 0.931±0.025 | (7.89±0.21) | | |
| 3-Methylheptane | n-Hexane | 1.532±0.070 | (7.62±0.35) | | |
| | Cyclohexane | 1.055±0.072 | (7.06±0.48) | (7.71±0.35) | -- |
| | n-Octane | 0.948±0.036 | (8.04±0.31) | | |
| n-Octane | n-Hexane | 1.680±0.038 | (8.35±0.19) | | 8.11[e] |
| | Cyclohexane | 1.157±0.027 | (7.74±0.18) | (8.03±0.32) | 8.42[m] |
| | n-Octane | -- | -- | | (8.48±0.10)[z] |
| Nonane | n-Hexane | 2.166±0.079 | (10.76±0.39) | | 9.70[e] |
| | | | | | 10.20[A] |
| | Cyclohexane | 1.449±0.028 | (9.69±0.19) | (10.50±0.26) | 10.70[w] |
| | n-Octane | 1.287±0.017 | (10.92±0.14) | | (11.30±1.10)[z] |
| n-Decane | n-Hexane | 2.371±0.073 | (11.78±0.36) | | 11.00[e] |
| | Cyclohexane | 1.668±0.022 | (11.16±0.15) | (11.81±0.18) | (12.9±1.00)[z] |
| | n-Octane | 1.401±0.006 | (11.88±0.05) | | |
| n-Undecane | n-Hexane | 2.371±0.073 | (11.78±0.36) | | 12.30[e] |
| | Cyclohexane | 1.668±0.022 | (11.16±0.15) | (12.78±0.53) | 12.50[B] |
| | n-Octane | 1.588±0.056 | (13.50±0.60) | | (11.90±2.00)[p] |

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309 a: Weighted average $k_{av} = (w_{ref1}k_{ref1} + w_{ref2}k_{ref2} + ...)/ (w_{ref1} + w_{ref2} + ...)$, where $w_{ref1} = 1/\sigma_{ref1}^2$, etc. The error,

310 $\sigma_{av}$, was given by: $\sigma_{av} = (1/\sigma_{ref1} + 1/\sigma_{ref2} + ...)^{-0.5}$.

311 b: (Demore and Bayes, 1999); c: (Mellouki et al., 1994); d: (Talukdar et al., 1994); e: (Atkinson and Arey,

312 2003); f: (Cox et al., 1980); g: (Morin et al., 2015); h: (Wilson et al., 2006); i: (Tully et al., 1986); j:

313 (Edney et al., 1986); k: (Perry et al., 1976); m: (Greiner, 1970a) ; n: (Donahue et al., 1998); o: (Harris and

314 Kerr, 1988); p: (Calvert et al., 2015); q: (Droege and Tully, 1987); r: (Singh et al., 2013); s: (Badra and

315 Farooq, 2015) u: (Sprengnether et al., 2009); t: (Anderson et al., 2004); v: (Greiner, 1970b), y: (Crawford

316 et al., 2011) ; z: (Li et al., 2006); L: (Shaw et al., 2020); w: (Atkinson et al., 1982); A: (Ferrari et al., 1996);

317 B: (Sivaramakrishnan and Michael, 2009); D: (Bejan et al., 2018); F: (Ballesteros et al., 2015).

## 3.2 Comparisons to structure-activity relationships

To evaluate the reliability of our experimental data, multiple comparisons were made between the obtained reaction rate constants and the SAR values of different experimental groups (Figure 4). As shown in Figure 4, most n-alkanes are fall into the shaded region, indicating a high level of agreement for $k_{OH}$ rate coefficients of most n-alkanes (experimental values) with the SAR values, particularly for C3-C11 n-alkanes (about within 10%). Although the measured values of n-butane and n-pentane were lower than the estimated values of Neeb (Neeb, 2000), the similar trend was observed when comparing our experimental data with the SAR values of (Wilson et al., 2006), and (Jenkin et al., 2018) (refer to Fig. 4 (c) and Fig. 4 (d)), suggesting a certain level of reliability in our results.

For branch alkanes, such as monomethyl branched alkanes (2-Methylpentane, 3-Methylpentane, 2-Methylhexane, 3-Methylhexane 2-Methylheptane and 3-Methylheptane), the obtained $k_{OH}$ values all fall within the shadow range. The results indicated a relatively consistent alignment between our experimental data and the SAR estimated data within a certain margin of error, particularly for the SAR values of Neeb and Jenkin et al. (within 8%). Nevertheless, there seemed to be something different for polymethyl branched alkanes, like 2,3-Dimethylbutane, the experimental data was about 25% higher than the estimated SAR values of Atkinson and Kwok et al. (1995) and Neeb (2000), especially 53% higher than that of Jenkin et al. (2018). This suggested a potential underestimation of $k_{OH}$ values of 2,3-dimethylbutane by these SAR estimation methods. It was also found that the $k_{OH}$ of this compound (at 298 K) could not be accurately estimated by Wilson et al. (Wilson et al., 2006) due to unknown reasons. Furthermore, compared with the SAR values of Atkinson and Kwok et al., the obtained data of 2,2-Dimethylbutane and 2,4-Dimethylpentane were relatively consistent with that, while compared with the estimated data of Neeb, Jenkin et al. and Wilson et al., our results are higher or lower by about 18% and 22%. It is worth noting that the obtained $k_{OH}$ value of 2,2,4-Trimethylpentane was about 23%, 16% and 17%, respectively, lower than the corresponding SAR values of Atkinson and Kwok et al., Neeb, and Jenkin et al. The results indicated that our understanding for the oxidation chemistry of these compounds is still limited, still need a lot of experimental data for alkanes with this structure to confirm.

For cyclic alkanes, such as cyclopentane and cyclohexane, the obtained $k_{OH}$ values in this study were approximately 32% and 15%, respectively, lower than the SAR values of Atkinson and Kwok et al., 1995; b. Neeb 2000; c. Jenkin et al. 2018. On the other hand, the obtained experimental values for methylcyclopentane and methylcyclohexane were similar to SAR values of Neeb and Wilson et al (within

348  5%) (Neeb, 2000; Wilson et al., 2006), However, compared with the SAR values of Atkinson and Kwok

349  et al. and Jenkin et al., this result is about 15% and 8% lower. The result suggested that the reaction

350  activity of these cycle-chain alkanes estimated with SAR methods (Kwok and Atkinson, 1995; Jenkin et

351  al., 2018) might be overestimated to varying degrees.
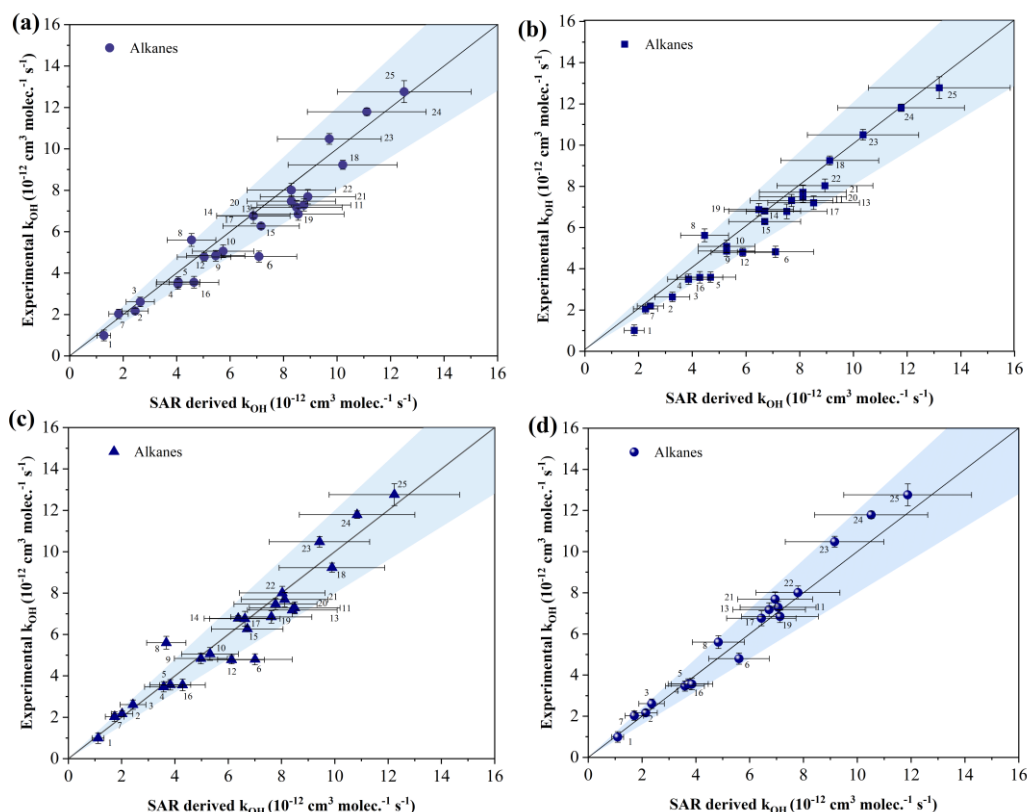
Figure 4. Measured Alkanes + OH rate coefficients plotted against SAR-derived rate coefficients for all compounds (a. (Kwok and Atkinson, 1995); b. (Neeb, 2000); c.  (Jenkin et al., 2018); d. (Wilson et al., 2006)). The shaded area demonstrates a 20 % uncertainty in the 1:1 black gradient line. The alkanes represented by serial number can be identified as follows: (1) Propane; (2) Isobutane; (3) n-Butane; (4) Isopentane; (5) n-pentane; (6) Cyclopentane; (7) 2,2-Dimethylbutane; (8) 2,3-Dimethylbutane; (9) 2-Methylpentane; (10) 3-Methylpentane; (11) Methylcyclopentane; (12) 2,4-Dimethylpentane; (13) Cyclohexane; (14) 2-Methylhexane; (15) 3-Methylhexane; (16) 2,2,4-Trimethylpentane; (17) n-Heptane; (18) Methylcyclohexane; (19) 2,3,4-Trimethylpentane; (20) 2-Methylheptane; (21) 3-Methylheptane; (22) n-Octane; (23) Nonane; (24) n-Decane; (25) n-Undecane.

## 3.3 Temperature dependence (273-323 K)

In order to study the relationship between temperature and reaction rate constant, this study carried out experiments in the tropospheric temperature range (273-323 K), and combined with the literature data

(the expert-recommended data from database for Version 2.1.0 of McGillen et al.) to study the kinetic temperature dependence of several alkanes in a wide temperature range. And n-hexane (Arrhenius expression: $k(T)$=(2.43±0.52)×10⁻¹¹ exp [–(481.2±60)/T] at 240-340 K was used as the reference compound. Since the research results at room temperature show that different bath gases have little effect on the reaction rate constant, only the temperature dependence of the reaction rate constant under the air system is considered here. Measured values for 24 C3-C10 alkanes were provided at different temperatures (273-323 K) in Table S3. And the preexponential factor A and activation energy $E_a$/R obtained by linear regression along with the values of the literature were listed in Table 2. The value of preexponential factor A increases with the increase of the number of carbon atoms, which is consistent with the law of its reactivity. Additionally, Arrhenius plots were linearly fitted using this data along with literature data. The following is a detailed analysis for several components that are important or temperature dependence data has been less or no studied, the Arrhenius plots are shown in Figure 4-5, other components are listed in the Supplement (Fig. S3-S15).

Table 2. Summary of Arrhenius Expression of the Reaction of OH radical with C3-C11 alkanes in this work and other studies.

| Alkanes | Temperature (K) | A-factor [a] (× 10⁻¹¹) | $E_a$/R[b] (K) | Technique [c] | Reference |
|---|---|---|---|---|---|
| Propane | 273-323 | 2.38±0.90 | 952±110 | RR/DP/GC-FID | this work |
| | 296-908 | 2.71±0.17 | 988±31 | AR/FP/LIF | (Bryukov et al., 2004) |
| | 227-428 | 1.29 | 730 | RR/DP/GC | (Demore and Bayes, 1999) |
| | 233-376 | 1.01 | 660 | AR/FP/LIF | (Talukdar et al., 1994) |
| | 300 - 390 | 1.12 | 692 | AR/EB/LIF | (Donahue et al., 1998) |
| n-Butane | 273-323 | 3.78±0.66 | 867±52 | RR/DP/GC-FID | this work |
| | 235 - 361 | 1.68 | 584 | RR/DP/GC | (Demore and Bayes, 1999) |
| | 300 - 390 | 1.34 | 513 | AR/EB/LIF | (Donahue et al., 1998) |
| | 231-378 | 1.18 | 470 | AR/ DF/LIF | (Talukdar et al., 1994) |
| | 294-509 | 1.88±0.09 | 617±18 | AR/ DF/LIF | (Droege and Tully, 1987) |
| | 298-420 | 1.76 | 559 | AR/ DF/RF | (Perry et al., 1976) |

| Compound | Temp range | $k$ | $E/R$ | Method | Reference |
|---|---|---|---|---|---|
| | 298-416 | 0.629 | 126 | AR-UV | (Gordon and Mulac, 1975) |
| | 273-323 | 0.90±0.05 | 310±17 | RR/DP/GC-FID | this work |
| | 233-364 | 1.94 | 494 | RR/DP/GC | (Demore and Bayes, 1999) |
| n-pentane | 300-390 | 2.97 | 608 | AR/EB/LIF | (Donahue et al., 1998) |
| | 224-372 | 2.45±0.21 | 516±25 | AR/FP/LIF | (Talukdar et al., 1994) |
| | 243-325 | -- | -- | RR/DP/GC | (Harris and Kerr, 1988) |
| | 240-896 | 5.06±0.45 | 602±30 | RR/DP/GC-FID | this work |
| | 290-1090 | 1.28±0.21 | 190 | Review | (Atkinson and Arey, 2003) |
| n-Heptane | 241-406 | 3.38±0.17 | 497±16 | RR/DF/MS | (Wilson et al., 2006) |
| | 240-340 | 2.25±0.14 | 293±37 | RR/DF/MS | (Crawford et al., 2011) |
| | 248-896 | 5.2±0.54 | 605±39 | AR/DF/LIF | (Morin et al., 2015) |
| | 298-500 | 0.0986 | 600 | Theory | (Cohen, 1991) |
| | 240-1080 | 5.07±0.97 | 543±61 | RR/DP/GC-FID | this work |
| | 240-340 | 2.27±0.21 | 296±27 | RR/DF/MS | (Li et al., 2006) |
| | 284-384 | 4.52±0.37 | 538±27 | RR/DF/MS | (Wilson et al., 2006) |
| n-Octane | 290-1080 | 1.78 | 235 | Review | (Atkinson and Arey, 2003) |
| | 296-497 | 2.57 | 332±65 | AR/FP/KS | (Greiner, 1970a) |
| | 298-1000 | 0.0986 | 600 | Theory | (Cohen, 1991) |
| Nonane | 273-323 | 5.29±0.63 | 520±35 | RR/DP/GC-FID | this work |
| | 240-340 | 4.35±0.49 | 411±32 | RR/DF/MS | (Li et al., 2006) |
| n-Decane | 273-323 | 5.78±0.49 | 499±25 | RR/DP/GC-FID | this work |
| | 240-340 | 2.26±0.28 | 160±36 | RR/DF/MS | (Li et al., 2006) |
| | 273-323 | 2.29±0.74 | 739±94 | RR/DP/GC-FID | this work |
| Isobutane | 300-390 | 0.626 | 321 | AR/EB/LIF | (Donahue et al., 1998) |
| | 213-372 | 0.572 | 293 | AR/FP/LIF | (Talukdar et al., 1994) |
| | 297-498 | 0.347 | 192 | AR/FP/GC | (Greiner, 1970a) |
| | 220-407 | 1.02±0.03 | 463±10 | RR/DF/MS | (Wilson et al., 2006) |
| Isopentane | 213-407 | 1.39±0.12 | 424±25 | RR/DP/GC-FID | this work |
| | 213-407 | 1.52 | 432 | RR/DP/GC | (Wilson et al., 2006) |
| | 273-323 | 3.67±0.63 | 619±51 | RR/DP/GC-FID | this work |
| Cyclopentane | 288-407 | 2.71 | 526 | RR/DP/GC | (Wilson et al., 2006) |
| | 240-340 | 2.43±0.50 | 481±58 | RR/DF/MS | (Singh et al., 2013) |

| | | | | | |
|---|---|---|---|---|---|
| | 273 - 423 | 2.57 | 498 | RR/DP/GC | (Demore and Bayes, 1999) |
| | 300-390 | 1.88 | 352 | AR/EB/LIF | (Donahue et al., 1998) |
| | 295-491 | 2.29±0.09 | 457±0.14 | AR/FP/LIF | (Droege and Tully, 1987) |
| | 273-323 | 3.62±0.59 | 522±48 | RR/DP/GC-FID | this work |
| Cyclohexane | 240-340 | 3.96±0.60 | 554±42 | RR/DF/MS | (Singh et al., 2013) |
| | 288-408 | 3.40 | 513 | RR/DP/GC | (Wilson et al., 2006) |
| | 230-1344 | 7.21±0.38 | 705±28 | RR/DP/GC-FID | this work |
| Methylcyclopentane | 230-1344 | 6.81±0.39 | 641±38 | AR/DF/LIF | (Sprengnether et al., 2009) |
| | 273-323 | 4.39±0.58 | 475±29 | RR/DP/GC-FID | this work |
| Methylcyclohexane | 273-343 | 1.85±0.27 | 195±20 | RR/DP/FTIR | (Bejan et al., 2018) |
| | 230-379 | 1.46±0.07 | 125±14 | AR/ DF/LIF | (Sprengnether et al., 2009) |
| | 273-323 | 3.53±1.28 | 899±106 | RR/DP/GC-FID | this work |
| | 240-330 | 3.37 | 809 | Review | (Atkinson and Arey, 2003) |
| 2,2-Dimethylbutane | 243-328 | -- | -- | RR/DP/GC | (Harris and Kerr, 1988) |
| | 254-1327 | 6.14±0.90 | 1023±76 | AR/DF/LIF | (Badra and Farooq, 2015) |
| | 273-1366 | 4.81±0.56 | 669±50 | RR/DP/GC-FID | this work |
| | 240-1220 | 3.98±0.41 | 579±50 | Review | (Atkinson and Arey, 2003) |
| 2,3-Dimethylbutane | 250-1366 | 4.75±0.71 | 664±77 | AR/DF/LIF | (Badra and Farooq, 2015) |
| | 220-1292 | 3.96±0.62 | 565±74 | Review | (Sivaramakrishnan and Michael, 2009) |
| | 273-323 | 2.03±0.17 | 452±24 | RR/DP/GC-FID | this work |
| 2,4-Dimethylpentane | 272-410 | 2.25 | 408 | RR/DP/GC | (Wilson et al., 2006) |
| | 896-1311 | 14.9±0.8 | 1533±55 | AR/DF/LIF | (Badra and Farooq, 2015) |
| 2-Methylpentane | 273-323 | 2.30±0.29 | 479±38 | RR/DP/GC-FID | This work |
| | 283-387 | 2.07 | 413 | RR/DP/GC | (Wilson et al., 2006) |
| | 273-323 | 2.44±0.39 | 511±17 | RR/DP/GC-FID | this work |
| 3-Methylpentane | 284-381 | 2.16 | 375 | RR/DP/GC | (Wilson et al., 2006) |
| | 297-1362 | 6.43±0.87 | 834±74 | AR/DF/LIF | (Badra and Farooq, 2015) |
| | 273-385 | 1.82±0.09 | 321±16 | RR/DP/GC-FID | this work |
| 2-Methylhexane | 230 - 385 | 1.21±0.07 | 171±16 | AR/ DF/LIF | (Sprengnether et al., 2009) |
| 3-Methylhexane | 273 - 323 | 2.53±1.45 | 575±161 | RR/DP/GC-FID | this work |

| | 230-379 | 1.42±1.52 | 628±85 | AR/ DF/LIF | (Sprengnether et al., 2009) |
|---|---|---|---|---|---|
| 2-Methylheptane | 273-323 | 3.93±1.33 | 536±102 | RR/DP/GC-FID | this work |
| 3-Methylheptane | 273-323 | 3.54±0.34 | 456±28 | RR/DP/GC-FID | this work |
| 2,2,4-Trimethylpentane | 273-323 | 1.61±0.22 | 499±40 | RR/DP/GC-FID | this work |
| | 240-500 | 1.62 | 443 | AR/ DF/LIF | (Atkinson, 1986) |
| | 230-385 | 1.54 | 456 | AR/ DF/LIF | (Atkinson, 2003) |
| 2,3,4-Trimethylpentane | 273-323 | 1.34±0.07 | 203±15 | RR/DP/GC-FID | this work |
| | 287-373 | 1.3 | 221 | RR/DP/GC | (Wilson et al., 2006) |

381  [a, b]The error bar was taken as $\sigma$.

382  [c]RR: relative rate; AR: absolute rate; DF: discharge flow; DP: direct photolysis; FP: flash photolysis; EB:

383  electron beam; UV: Ultraviolet; GC: gas chromatography; FID: flame ionization detection; LIF: laser

384  induced fluorescence; FTIR: fourier transform infrared spectrometer; MS: mass spectrometry; KS:

385  kinetic-spectroscopy.

386  **A. OH+ n-Octane.** Figure 5 (a) exhibits the Arrhenius plot for the reaction between n-Octane and

387  OH radicals, covering a temperature range of 240 to 1080 K. Within the experimental temperature range

388  (273-323 K), our data align well with previous studies. Fit our data to expert-evaluated data (manually

389  entered data from multiple sources), the derived Arrhenius expressions are as follows:

390  $k_{n-Octane}$(T)=(5.07±0.97)×10$^{-11}$exp [-(543±61)/T] cm$^3$ molecule$^{-1}$ s$^{-1}$. This result agree well with the

391  Arrhenius expression of (4.52±0.37)×10$^{-11}$exp [-(538±27)/T] cm$^3$·molecule$^{-1}$·s$^{-1}$ reported by Wilson et al.

392  (Wilson et al., 2006) between 284 and 384 K and (4.95±0.87)×10$^{-11}$exp [-(531±56)/T] recommended

393  Arrhenius formula obtained by experts' evaluation of data processing, but contrast the expressions of

394  (2.27±0.21)×10$^{-11}$exp [-(296±27)/T] cm$^3$·molecule$^{-1}$·s$^{-1}$ reported by Li et al. between 240 and 340 K (Li

395  et al., 2006) and (2.57)×10$^{-11}$exp[-(332±65)/T] cm$^3$·molecule$^{-1}$·s$^{-1}$ reported by Greiner (Greiner, 1970a)

396  between 296 and 497 K. By comparison, our data are highly consistent with the data recommended by

397  experts. The obtained Arrhenius expression more accurately represents the relationship between the

398  reaction rate constant of octane and OH radicals and temperature in a wide temperature range, which has

399  certain reference significance. Further investigations are necessary to understand the discrepancies

400  amongst these studies.

401  **B. OH+ n-Heptane.** The Arrhenius plot in Fig. 5 (b) displays the reaction between n-Heptane and

402  OH radicals in the air systems, covering a temperature range of 240 to 896 K. As shown in the figure,

within the experimental temperature range (273-323 K), our data are highly similar to previous studies. By fitting our data and recommended data from multiple sources to the Arrhenius equation, the resulting Arrhenius expressions are as follows: $k_{n\text{-}Heptane}$(T)=(5.06±0.45)×$10^{-11}$exp [-(602±30)/T] cm$^3$ molecule$^{-1}$ s$^{-1}$. This result agree well with the Arrhenius expression of (5.20±0.54)×$10^{-11}$exp [-(605±39)/T] cm$^3$·molecule$^{-1}$·s$^{-1}$ reported by Morin et al. (Morin et al., 2015) between 248 and 896 K. The recommended Arrhenius equation for the reaction of OH radical and n-Heptane is in the form $k$ (T) =3.84×$10^{-12}$*exp(148/T) * (T/300)$^{1.79}$. Rearrange the fitting data to get the Arrhenius expression in the form of $k$ (T) =(4.82±0.43)×$10^{-11}$exp [-(600±31)/T] cm$^3$ molecule$^{-1}$ s$^{-1}$. Compared with the Arrhenius expression recommended in the literature, the preexponential factor A (5.01±0.42) of this work is agree well with the one (4.82±0.43) of recommended (the unit is $10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$). However, the activation energy Ea/R of this work is about 60% higher than the recommended data.

**C. OH+ Isopentane.** As Fig. 5 (c), isopentane was extensively studied over a temperature range (213-407 K). As far as we know, at present, only Wilson et al. has reported this compound in the range of 213-407 K (Wilson et al., 2006). Within the experimental temperature range (273-323 K), our data are consistent with Wilson et al. (273-323 K), especially in the low temperature range. The Arrhenius expression at 213-407 K obtained by fitting our data and those of Wilson et al. is as follows: $k_{Isopentane}$(T)=(1.39±0.12)×$10^{-11}$exp [-(424±25)/T] cm$^3$ molecule$^{-1}$ s$^{-1}$. The results are similar to the relative experimental results of Wilson et al. (1.52±0.21)×$10^{-11}$exp [-(432±27)/T] cm$^3$ molecule$^{-1}$ s$^{-1}$.

**D. OH+ 2,3-Dimethylbutane.** Figure 5 (d) shows the Arrhenius plot for the reaction of 2,3-Dimethylbutane with OH radicals over the temperature range of 273 K to 1366 K. The temperature-dependent values obtained in this study at high temperature (313-323 K) align closely with those reported by Badra and Farooq (Badra and Farooq, 2015), who used the absolute rate technique, as well as the work of Sivaramakrishnan and Michael with a three-parameter fit (Sivaramakrishnan and Michael, 2009). However, the data obtained at 273-293 K in this work are highly consistent with the reviewed data from Atkinson and Arey (Atkinson and Arey, 2003). Linear regression applied to our data and high temperature data in the literature (at 273-1366 K) yields the Arrhenius expression as follows: $k_{2,3\text{-}Dimethylbutane}$(T) =(4.81±0.56)×$10^{-12}$exp [-(669±50)/T] cm$^3$ molecule$^{-1}$ s$^{-1}$. This result agrees well with the Arrhenius expression of (4.75±0.71)×$10^{-11}$exp [-(664±77)/T] cm$^3$·molecule$^{-1}$·s$^{-1}$ reported by Badra and Farooq (Badra and Farooq, 2015).
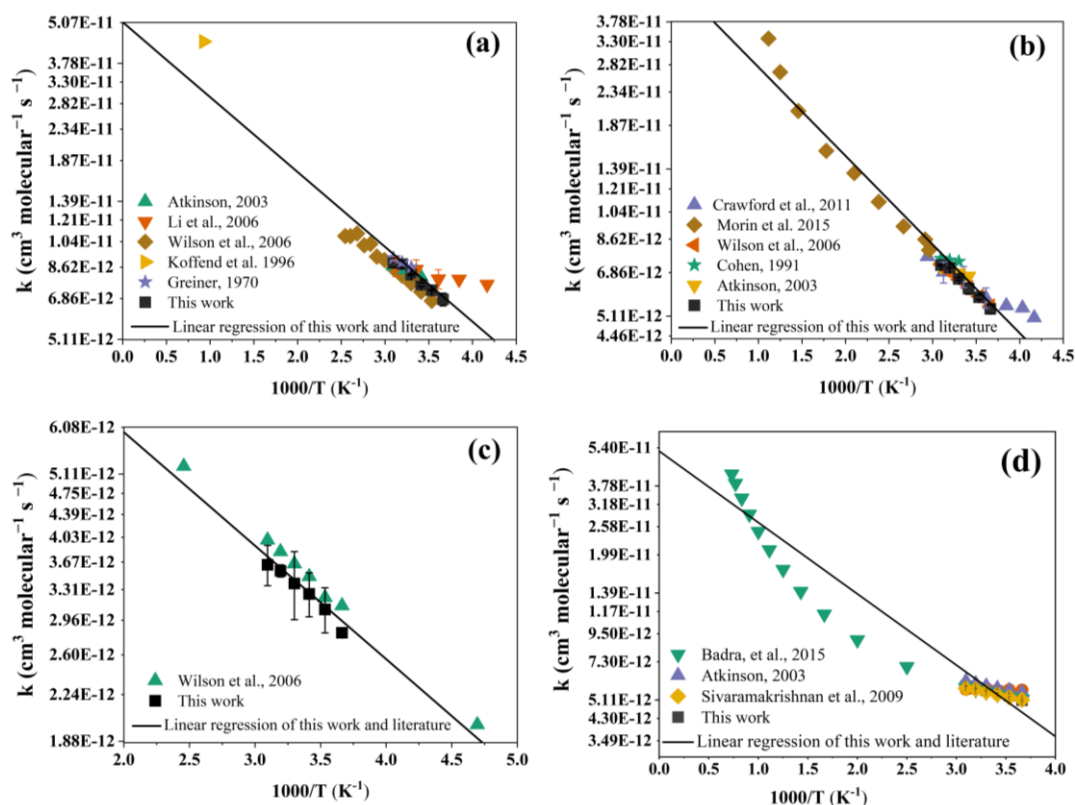
Figure 5. Arrhenius plots for the reaction of n-Octane (a), n-Heptane (b), Isopentane (c) and 2,3-Dimethylbutane (d) with OH radical in wide temperature range along with available literature data. The error bar was taken as 2σ.

**E. OH+ Methylcyclopentane (2-Methylhexane).** Figure 6 (a) and (b) illustrate the Arrhenius plot for the reaction of methylcyclopentane (230-1344 K) and 2-methylhexane (273-385) with OH radical. Literature data from Sprengnether et al. (Sprengnether et al., 2009) and Anderson et al. (Anderson et al., 2004) are available for comparison purposes. Notably, for methylcyclopentane, Anderson et al. (Anderson et al., 2004) reported absolute data that is 26% higher than the relative data obtained in this study at 298 K. However, this difference falls within the margin of error. The absolute data from Sprengnether et al. (Sprengnether et al., 2009) is slightly higher, ranging from 10% to 20%, compared to this study. The experimental data obtained at 273-323 K are fitted with multi-party literature data, especially the data from Sivaramakrishnan and Michael at high temperature (859-1344 K), the resulting Arrhenius expression is as follows: $k_{Methylcyclopentane}$(T) =(7.21±0.38)×10$^{-11}$exp [-(705±28)/T] cm$^3$ molecule$^{-1}$ s$^{-1}$. Similar to the treatment of Arrhenius equation for n-Heptane, the result is highly consistent with the expert-evaluated Arrhenius expression of methylcyclopentane ($k_{Methylcyclopentane}$(T) = (6.81±0.39)×10$^{-11}$exp [-(641±38)/T] cm$^3$ molecule$^{-1}$ s$^{-1}$), indicating that the data obtained has a certain degree of reliability.

449 At present, the research on the temperature dependence of 2-Methylhexane only includes the measured

450 reaction rate constant with OH radical of Sprengnether et al. by absolute rate technique at 230-385 K. The

451 Arrhenius expression obtained by fitting our data with Sprengnether et al's data at 230-385 K is as follows:

452 $k_{2\text{-}Methylhexane}(T) =(1.82\pm0.09)\times10^{-11}\exp[-(321\pm16)/T]$ cm$^3$ molecule$^{-1}$ s$^{-1}$. Expert-evaluated Arrhenius

453 expression is $k_{2\text{-}Methylhexane}(T) =(1.21\pm0.07)\times10^{-11}\exp[-(171\pm16)/T]$ cm$^3$ molecule$^{-1}$ s$^{-1}$. Through

454 comparison, it can be clearly seen that the two are highly consistent, indicating that the obtained Arrhenius

455 expression has certain reference value. To the best of our knowledge, this is the first investigation of the

456 temperature-dependent kinetics for the reaction of methylcyclopentane and 2-methylhexane with OH

457 radicals utilizing the relative rate technique.

458 **F. OH+ 3-Methylheptane.** In Figure 6 (c), the Arrhenius plot presents the reaction between 3-

459 Methylheptane and OH radicals, spanning a temperature range of 273 to 323 K. A linear regression

460 analysis of our data yields the following Arrhenius expressions:

461 $k_{3\text{-}Methylheptane}(T) =(2.72\pm0.34)\times10^{-11}\exp[-(456\pm28)/T]$ cm$^3\cdot$molecule$^{-1}\cdot$s$^{-1}$. We believe this study to be

462 the first investigation of the temperature-dependent kinetics for the reaction between 3-Methylheptane

463 and OH radicals. The only previous study on this reaction, reported by Shaw et al. (Shaw et al., 2020)

464 utilizing the relative rate method in nitrogen at 323 K, demonstrates significantly higher data (>65%)

465 compared to our results. Possible explanations for this discrepancy lie in the different reference

466 compounds used and potential sample loss during sampling in the enrichment tube in Shaw et al.

467 **G. OH+ 3-Methylhexane (Figure 6 (d)).** This is the first temperature-dependence relative data. It

468 can be seen from the figure that this data is this data is significantly lower by approximately 80%

469 compared to the absolute data. The Arrhenius expression at 273-323 K is as follows:

470 $k_{3\text{-}Methylhexane}(T) =(2.53\pm1.45)\times10^{-11}\exp[-(575\pm161)/T]$ cm$^3\cdot$molecule$^{-1}\cdot$s$^{-1}$

471 **H. OH+ 2-Methylheptane (Figure 6 (e)).** There are no previous temperature dependence data on

472 this compound. Similar to 3-Methylhexane, this data is lower by approximately 37% compared to Shaw

473 et al. at room temperature. Furthermore, the data obtained at 273-283 K shows an increase. Within the

474 range of 293-323 K, the obtained Arrhenius expression is as follows:

475 $k_{2\text{-}Methylheptane}(T) =(3.93\pm1.33)\times10^{-11}\exp[-(536\pm102)/T]$ cm$^3\cdot$molecule$^{-1}\cdot$s$^{-1}$.
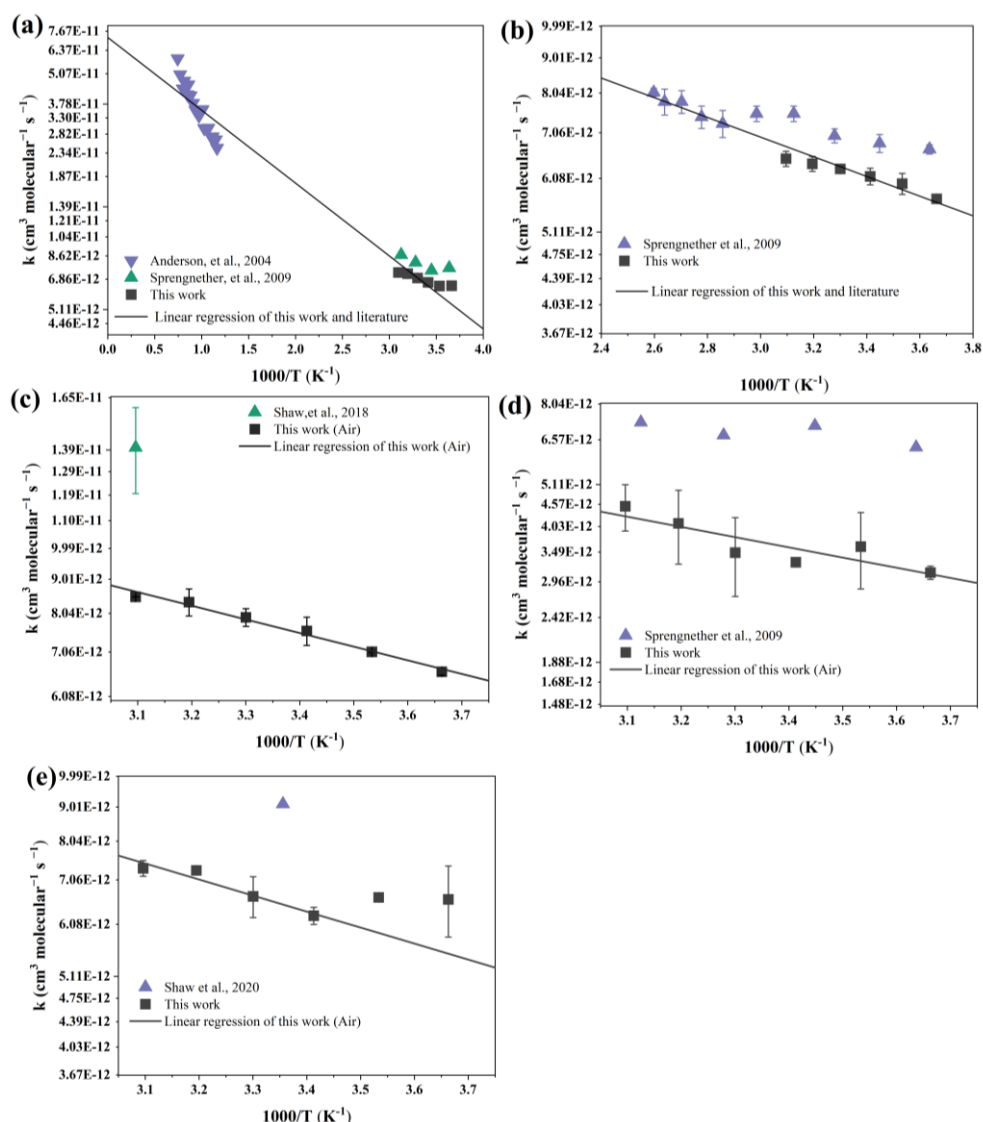
Figure 6. Arrhenius plots for the reaction of Methylcyclopentane (a), 2-Methylhexane (b), 3-Methylhepane (c), 3-Methylhexane (d) and 2-Methylhepane (e) with OH radical along with available literature data. The error bar was taken as 2σ.

## 3.4 Correlation between the rate coefficients of the reaction of alkanes with OH radicals and chlorine atoms

Figure 7 presents a log–log correlation plot between the Cl atoms and OH radical rate coefficients with the series of C3-C11 studied above. A very clear correlation ($R^2$ =0.86) described by the relation $\log_{10}[k_{(Cl+alkanes)}] = 0.569 \times \log_{10}[k_{(OH+alkanes)}]$-3.111 was obtained. Although the correlation between propane and isobutane is relatively discrete, the reactivity of saturated alkanes with OH radicals and chlorine atoms is still clearly related to the saturated alkane series. In addition, the log–log correlation for the series of saturated alkanes with these two oxidants presented by Calvert et al. (2011) described

by the relation $\log_{10}[k_{(Cl+alkanes)}] = 0.521 \times \log_{10}[k_{(OH+alkanes)}]\text{-}3.670$ with ($R^2$=0.85) is in better agreement with the log–log correlations obtained in this study for saturated alkanes. This correlation can be utilized to predict rate coefficients for unmeasured reactions, such as the reaction of 2,2,3-trimethylpentane with chlorine atoms.
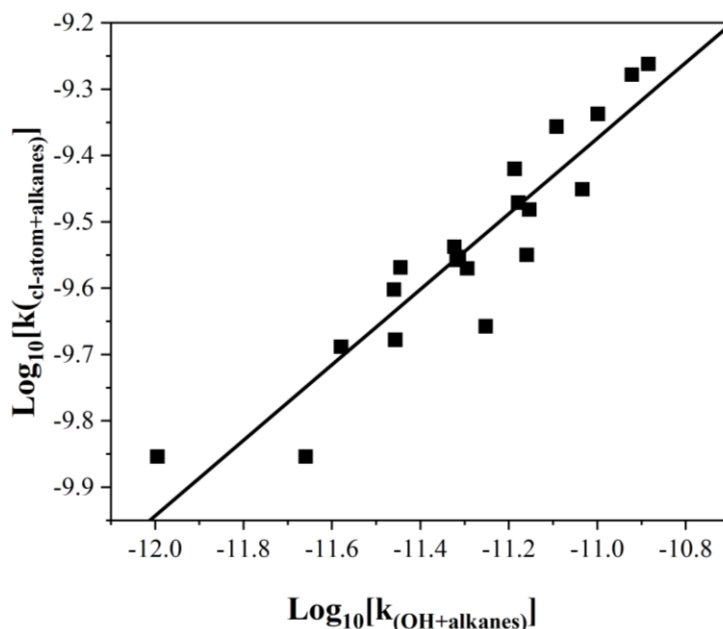
Figure 7. Double logarithmic plot ($\log_{10}$) of the rate coefficients for the reaction of Cl-atoms versus the reaction of OH radicals with the saturated alkanes (C3-C11 alkanes studied above). The solid line represents the unweighted least-squares fit to the data.

## 3.5 Atmospheric lifetime and implications

The atmospheric lifetime of alkanes in the troposphere can be estimated using the following formula:

$$\tau_{alkane} = 1/(k_{alkane+OH}[OH])$$

where $\tau_{alkane}$ is the atmospheric lifetime of the alkane due to OH removal, $k_{alkane+OH}$ is the rate constant for the reaction of the alkane with OH radical at the typical tropospheric temperature of 298 K, and [OH] is the atmospheric concentrations of the hydroxyl radicals. The average tropospheric hydroxyl radical concentration has been previously reported in the literature as $1 \times 10^6$ molecules $cm^{-3}$ (Li et al., 2018). Using the $k_{alkane+OH}$ (298 K) values determined in the present work, the atmospheric lifetime for 25 alkanes was estimated and listed on the Table S4. As can be seen from the table, the atmospheric lifetime of C3-C11 alkanes reacting with OH radicals are about 1-11 days. As the carbon chain grows, the atmospheric lifetime seems to reduce, especially for long-chain alkanes with carbon atoms of 8-11, the residence time

in the atmosphere is only about 1 day. They are emitted into the air and degraded quickly to generate alkyl radicals, which are immediately converted into alkyl peroxy radicals by reacting with abundant $O_2$ in the atmosphere. The subsequent reaction of alkyl peroxyl radicals enhances the conversion of NO to $NO_2$ by $HO_2$ radicals, leading to the production of tropospheric ozone. For short-chain alkanes that stay in the atmosphere for a long time, such as propane, the lifetime is 11d. It should be noted that because the OH concentration is the global average estimated concentration, the applicability of the lifetime may be different in the atmosphere with different OH radical concentrations.

# 4. Conclusions

The use of the multivariate relative rate method in this study allowed for the simultaneous determination of reaction rate constants of C3-C11 alkanes and OH radicals in different bath gases, which significantly improved the efficiency of determination. New data and Arrhenius expressions for the reaction of Methylcyclopentane, 2-Methylhepane, 3-Methylheptane, 2-Methylhexane and 3-Methylhexane with OH radicals were obtained for the first time in the temperature range of 273-323 K, expanding the existing database. The measured relative rate constants of air bath gases in the temperature range studied were found to be highly consistent with values obtained in $N_2$, suggesting that the rate constants obtained in this experiment can reasonably represent the rate constants in the actual atmosphere. The structure-additivity method for rate constant estimation is mostly consistent for the prediction of $K_{OH}$ (298 K) for the studied n-alkanes, but its methodology and parameters do not seem to be able to reasonably estimate the rate constant of 2,3-dimethylbutane. Additionally, there is a big discrepancy in the case of several cycloalkanes (cyclopentane, methylcyclopentane, cyclohexane) and branch alkanes (2,2,4-Trimethylpentane) with this experiment for estimation parameters' overestimate. There is a reasonable suspicion that this method is still lacking some additional factors.

# Data availability

Raw data are available upon request.

## Author contributions

YM and CL planned the campaign; YX performed the measurements; YX, CL, YM and XL analyzed the data; YX and CL wrote the manuscript draft. SX and JL provided technical support.

## Competing interests

The authors declare that they have no conflict of interest.

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## References

Andersen, M. P. S., Hurley, M. D., Ball, J. C., Schneider, W. F., Wallington, T. J., and Nielsen, O. J.: $CF_3CH(ONO)CF_3$: synthesis, IR spectrum, and use as OH radical source for kinetic and mechanistic studies, Int. J. Chem. Kinet., 35, 159-165, https://doi.org/10.1002/kin.10116, 2003.

Anderson, R. S., Huang, L., Iannone, R., Thompson, A. E., and Rudolph, J.: Carbon kinetic isotope effects in the gas phase reactions of light alkanes and ethene with the OH radical at $296 \pm 4$ K, J. Phys. Chem. A, 108, 11537-11544, https://doi.org/10.1021/jp0472008, 2004.

Atkinson, R.: Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds under atmospheric conditions, Chem. Rev., 86, 69-201, https://doi.org/10.1021/cr00071a004, 1986.

Atkinson, R.: Atmospheric chemistry of VOCs and NOx, Atmos. Environ., 34, 2063-2101, https://doi.org/10.1016/S1352-2310(99)00460-4, 2000.

Atkinson, R.: Kinetics of the gas-phase reactions of OH radicals with alkanes and cycloalkanes, Atmos. Chem. Phys., 3, 2233-2307, https://doi.org/10.5194/acp-3-2233-2003, 2003.

Atkinson, R. and Arey, J.: Atmospheric degradation of volatile organic compounds, Chem. Rev., 103, 4605-4638, https://doi.org/10.1021/cr0206420, 2003.

Atkinson, R., Aschmann, S. M., Carter, W. P. L., Winer, A. M., and Pitts Jr., J. N.: Kinetics of the reactions

of OH radicals with n-alkanes at 299 ± 2 K, Int. J. Chem. Kinet., 14, 781-788, https://doi.org/10.1002/kin.550140706, 1982.

Badra, J. and Farooq, A.: Site-specific reaction rate constant measurements for various secondary and tertiary H-abstraction by OH radicals, Combust. Flame, 162, 2034-2044, https://doi.org/10.1016/j.combustflame.2015.01.001, 2015.

Ballesteros, B., Ceacero-Vega, A. A., Jimenez, E., and Albaladejo, J.: Atmospheric reactions of methylcyclohexanes with Cl atoms and OH radicals: determination of rate coefficients and degradation products, Environ. Sci. Pollut. Res. Int., 22, 4806-4819, https://doi.org/10.1007/s11356-014-2901-0, 2015

Bejan, I. G., Winiberg, F. A. F., Mortimer, N., Medeiros, D. J., Brumby, C. A., Orr, S. C., Kelly, J., and Seakins, P. W.: Gas-phase rate coefficients for a series of alkyl cyclohexanes with OH radicals and Cl atoms, Int. J. Chem. Kinet., 50, 544-555, https://doi.org/10.1002/kin.21179, 2018.

Bryukov, M. G., Knyazev, V. D., Lomnicki, S. M., McFerrin, C. A., and Dellinger, B.: Temperature-dependent kinetics of the gas-phase reactions of OH with $Cl_2$, $CH_4$, and $C_3H_8$, J. Phys. Chem. A, 108, https://doi.org/10.1021/jp047340h, 2004.

Calvert, J. G., Orlando, J. J., Stockwell, W. R., and Wallington, T. J.: The mechanisms of reactions influencing atmospheric ozone, Oxford University Press, Incorporated, New York, United States, 609 pp., ISBN 9780190233037, 2015.

Cohen, N.: Are reaction rate coefficients additive? Revised transition state theory calculations for OH + alkane reactions, Int. J. Chem. Kinet., 23, 397-417, https://doi.org/10.1002/kin.550230506, 1991.

Cox, R. A., Derwent, R. G., and Williams, M. R.: Atmospheric photooxidation reactions. rates, reactivity, and mechanism for reaction of organic compounds with hydroxyl radicals, Environ. Sci. Technol., 14, 57-61, https://doi.org/10.1021/es60161a007, 1980.

Crawford, M. A., Dang, B., Hoang, J., and Li, Z.: 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, Int. J. Chem. Kinet., 43, 489-497, https://doi.org/10.1002/kin.20574, 2011.

Darnall, K. R., Atkinson, R., and Pitts, J. N.: Rate constants for the reaction of the OH radical with selected alkanes at 300 K, J. Phys. Chem., 82, 1581-1584, https://doi.org/10.1021/j100503a001, 1978.

DeMore, W. and Bayes, K.: Rate constants for the reactions of hydroxyl radical with several alkanes, cycloalkanes, and dimethyl ether, J. Phys. Chem. A, https://doi.org/103, 2649-2654, 1999.

Donahue, N. M., Anderson, J. G., and Demerjian, K. L.: New rate constants for ten OH alkane reactions

from 300 to 400 K: an assessment of accuracy, J. Phys. Chem. A, https://doi.org/102, 3121-3126, 1998.

Droege, A. T. and Tully, F. P.: Hydrogen-atom abstraction from alkanes by hydroxyl radical. 6. cyclopentane and cyclohexane, J. Phys. Chem., 91, https://doi.org/1222-1225, 1987.

Dunmore, R. E., Hopkins, J. R., Lidster, R. T., Lee, J. D., Evans, M. J., Rickard, A. R., Lewis, A. C., and Hamilton, J. F.: Diesel-related hydrocarbons can dominate gas phase reactive carbon in megacities, Atmos. Chem. Phys., 15, 9983-9996, https://doi.org/10.5194/acp-15-9983-2015, 2015.

Edney, E., Kleindienst, T., and Corse, E.: Room temperature rate constants for the reaction of OH with selected chlorinated and oxygenated hydrocarbons, Int. J. Chem. Kinet., 18, 1355-1371, https://doi.org/10.1002/kin.550181207, 1986.

Ferrari, C., Roche, A., Jacob, V., Foster, P., and Baussand, P.: Kinetics of the reaction of OH radicals with a series of esters under simulated conditions at 295 K, Int. J. Chem. Kinet., 28, 609-614, https://doi.org/10.1002/(sici)1097-4601(1996)28:8<609::aid-kin6>3.0.co;2-z, 1996.

Finlayson-Pitts, B. J. and Pitts, J. N., Jr.: Tropospheric air pollution: ozone, airborne toxics, polycyclic aromatic hydrocarbons, and particles, Science (New York, N.Y.), 276, https://doi.org/1045-1052, 10.1126/science.276.5315.1045, 1997.

Finlaysonpitts, B. J., Hernandez, S. K., and Berko, H. N.: A new dark source of the gaseous hydroxyl radical for relative rate measurements, J. Phys. Chem., 97, 1172-1177, https://doi.org/10.1021/j100108a012, 1993.

Fiore, A. M., Horowitz, L. W., Purves, D. W., Levy, H., Evans, M. J., Wang, Y. X., Li, Q. B., and Yantosca, R. M.: Evaluating the contribution of changes in isoprene emissions to surface ozone trends over the eastern United States, J. Geophys. Res.-Atmos., 110, 18, https://doi.org/10.1029/2004jd005485, 2005.

Goldstein, A. H. and Galbally, I. E.: Known and unexplored organic constituents in the earth's atmosphere, Environ. Sci. Technol., 41, http://doi.org/1514-1521, 10.1021/es072476p, 2007.

Gordon, S. and Mulac, W.: Reaction of the OH (X• 71') radical produced by the pulse radiolysis of water vapor Int, J. Chern. Kinet.,(Syrnp. 1), 289, 299, 1975.

Gorse, R. A. and Volman, D. H.: Photochemistry of the gaseous hydrogen peroxide—carbon monoxide system. II: Rate constants for hydroxyl radical reactions with hydrocarbons and for hydrogen atom reactions with hydrogen peroxide, J. Photochem., 3, 115-122, https://doi.org/10.1016/0047-2670(74)80011-0, 1974.

Greiner, N. R.: Hydroxyl-Radical Kinetics by Kinetic Spectroscopy. II. Reactions with $C_2H_6$, $C_3H_8$, and

iso-C$_4$H$_{10}$ at 300°K, J. Chem. Phys., 46, 3389-3392, https://doi.org/10.1063/1.1841228, 1967.

Greiner, N. R.: Hydroxyl radical kinetics by kinetic spectroscopy. VI. Reactions with Alkanes in the range 300–500°K, J. Chem. Phys., 53, 1070-&, https://doi.org/10.1063/1.1674099, 1970a.

Greiner, N. R.: Comparison of the kinetics of alkane H-atom abstraction by methyl and hydroxyl radicals, J. Chem. Phys., 53, 1285-1287, https://doi.org/10.1063/1.1674134, 1970b.

Guenther, A.: The contribution of reactive carbon emissions from vegetation to the carbon balance of terrestrial ecosystems, Chemosphere, 49, 837-844, https://doi.org/10.1016/s0045-6535(02)00384-3, 2002.

Harris, S. J. and Kerr, J. A.: Relative Rate measurements of some reactions of hydroxyl radicals with alkanes studied under atmospheric conditions, Int. J. Chem. Kinet., 20, 939-955, https://doi.org/10.1002/kin.550201203, 1988.

Jenkin, M. E., Valorso, R., Aumont, B., Rickard, A. R., and Wallington, T. J.: Estimation of rate coefficients and branching ratios for gas-phase reactions of OH with aliphatic organic compounds for use in automated mechanism construction, Atmos. Chem. Phys., 18, 9297-9328, https://doi.org/10.5194/acp-18-9297-2018, 2018.

Kwok, E. S. and Atkinson, R.: Estimation of hydroxyl radical reaction rate constants for gas-phase organic compounds using a structure-reactivity relationship: an update, Atmos. Environ., 29, 1685-1695, https://doi.org/10.1016/1352-2310(95)00069-b, 1995.

Lewis, A. C., Carslaw, N., Marriott, P. J., Kinghorn, R. M., Morrison, P., Lee, A. L., Bartle, K. D., and Pilling, M. J.: A larger pool of ozone-forming carbon compounds in urban atmospheres, Nature, 405, 778-781, https://doi.org/10.1038/35015540, 2000.

Li, Z. J., Singh, S., Woodward, W., and Dang, L.: Kinetics study of OH radical reactions with n-octane, n-nonane, and n-decane at 240-340 K using the relative rate/discharge flow/mass spectrometry technique, J. Phys. Chem. A, 110, 12150-12157, https://doi.org/10.1021/jp0638134, 2006.

Liang, S., Gao, S., Wang, S., Chai, W., Chen, W., and Tang, G.: Characteristics, sources of volatile organic compounds, and their contributions to secondary air pollution during different periods in Beijing, China, Sci. Total. Environ., 858, 159831, https://doi.org/10.1016/j.scitotenv.2022.159831, 2023.

Ling, Z. H. and Guo, H.: Contribution of VOC sources to photochemical ozone formation and its control policy implication in Hong Kong, Environ. Sci. Policy, 38, 180-191, https://doi.org/10.1016/j.envsci.2013.12.004, 2014.

Liu, C. T., Mu, Y. J., Zhang, C. L., Zhang, Z. B., Zhang, Y. Y., Liu, J. F., Sheng, J. J., and Quan, J. N.:

Development of gas chromatography-flame ionization detection system with a single column and liquid nitrogen-free for measuring atmospheric C2-C12 hydrocarbons, J. Chromatogr. A, 1427, 134-141, https://doi.org/10.1016/j.chroma.2015.11.060, 2016.

Mellouki, A., Téton, S., Laverdet, G., Quilgars, A., and Le Bras, G.: Kinetic studies of OH reactions with $H_2O_2$, $C_3H_8$ and $CH_4$ using the pulsed laser photolysis-laser induced fluorescence method, J. Chim. Phys. PCB., 91, 473-487, https://doi.org/10.1051/jcp/1994910473, 1994.

Morin, J., Romanias, M. N., and Bedjanian, Y.: Experimental study of the reactions of OH radicals with Propane, n-Pentane, and n-Heptane over a wide temperature range, Int. J. Chem. Kinet., 47, 629-637, https://doi.org/10.1002/kin.20936, 2015.

Neeb, P.: Structure-reactivity based estimation of the rate constants for hydroxyl radical reactions with hydrocarbons, J. Atmos. Chem., 35, 295-315, https://doi.org/10.1023/a:1006278410328, 2000.

Overend, R. P., Paraskevopoulos, G., and Cvetanovic, R. J.: Rates of OH Radical Reactions. I. Reactions with $H_2$, $CH_4$, $C_2H_6$, and $C_3H_8$ at 295 K, Can. J. Chem., https://doi.org/10.1139/v75-482, 1975.

Perry, R. A., Atkinson, R., and Pitts, J. N.: Rate constants for the reaction of OH radicals with nbutane over the temperature range 297–420°K, J. Chem. Phys., 64, 5314-5316, https://doi.org/10.1063/1.432167, 1976.

Phan, M. and Li, Z. J.: Kinetics Study of the Reactions of OH with n-Undecane and n-Dodecane Using the RR/DF/MS Technique, J. Phys. Chem. A, 121, 3647-3654, https://doi.org/10.1021/acs.jpca.7b01512, 2017.

Shaw, J. T., Rickard, A. R., Newland, M. J., and Dillon, T. J.: Rate coefficients for reactions of OH with aromatic and aliphatic volatile organic compounds determined by the multivariate relative rate technique, Atmos. Chem. Phys., 20, 9725-9736, https://doi.org/10.5194/acp-20-9725-2020, 2020.

Shaw, J. T., Lidster, R. T., Cryer, D. R., Ramirez, N., Whiting, F. C., Boustead, G. A., Whalley, L. K., Ingham, T., Rickard, A. R., Dunmore, R. E., Heard, D. E., Lewis, A. C., Carpenter, L. J., Hamilton, J. F., and Dillon, T. J.: A self-consistent, multivariate method for the determination of gas-phase rate coefficients, applied to reactions of atmospheric VOCs and the hydroxyl radical, Atmos. Chem. Phys., 18, 4039-4054, https://doi.org/10.5194/acp-18-4039-2018, 2018.

Shi, B., Wang, W., Zhou, L., Li, J., Wang, J., Chen, Y., Zhang, W., and Ge, M.: Kinetics and mechanisms of the gas-phase reactions of OH radicals with three C15 alkanes, Atmos. Environ., 207, 75-81, https://doi.org/10.1016/j.atmosenv.2019.03.028, 2019.

Singh, S., de Leon, M. F., and Li, Z. J.: Kinetics Study of the Reaction of OH Radicals with $C_5$-$C_8$ Cycloalkanes at 240-340 K using the Relative Rate/Discharge Flow/Mass Spectrometry Technique, J. Phys. Chem. A, 117, 10863-10872, https://doi.org/10.1021/jp406923d, 2013.

Sivaramakrishnan, R. and Michael, J. V.: Rate constants for OH with selected large alkanes: shock-tube measurements and an improved group scheme, J. Phys. Chem. A, 113, 5047-5060, https://doi.org/10.1021/jp810987u, 2009

Sprengnether, M. M., Demerjian, K. L., Dransfield, T. J., Clarke, J. S., Anderson, J. G., and Donahue, N. M.: Rate constants of nine C6-C9 alkanes with OH from 230 to 379 K: chemical tracers for OH, J. Phys. Chem. A, 113, 5030-5038, https://doi.org/10.1021/jp810412m, 2009.

Sun, J., Wu, F. K., Hu, B., Tang, G. Q., Zhang, J. K., and Wang, Y. S.: VOC characteristics, emissions and contributions to SOA formation during hazy episodes, Atmos. Environ., 141, 560-570, https://doi.org/10.1016/j.atmosenv.2016.06.060, 2016.

Talukdar, R. K., Mellouki, A., Gierczak, T., Barone, S., Chiang, S. Y., and Ravishankara, A. R.: Kinetics of the reactions of OH with alkanes, Int. J. Chem. Kinet., 26, 973-990, https://doi.org/10.1002/kin.550261003, 1994.

Tully, F. P., Goldsmith, J. E. M., and Droege, A. T.: Hydrogen-atom abstraction from alkanes by OH. 4. Isobutane, J. Phys. Chem., 90, 5932-5937, https://doi.org/10.1021/j100280a095, 1986.

Wilson, E. W., Hamilton, W. A., Kennington, H. R., Evans, B., Scott, N. W., and DeMore, W. B.: Measurement and estimation of rate constants for the reactions of hydroxyl radical with several alkanes and cycloalkanes, J. Phys. Chem. A, 110, https://doi.org/3593-3604, 10.1021/jp055841c, 2006.