Rate coefficients for the reactions of OH radical with C_3-C_{11} alkanes determined by the relative rate technique

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Abstract: Rate coefficients for the reactions of OH radicals with C_3-C_{11} alkanes were determined using the multivariate relative rate technique. A total of 25 relative rate coefficients at room temperature and 24 Arrhenius expressions in the temperature range of 273-323 K were obtained. Notably, a new room temperature relative rate coefficient 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 of Atkinson and Kwok, Neeb, Wilson, Jenkin, and McGillen, the three cyclo-alkanes (cyclopentane, methylcyclopentane, cyclohexane) and one branched alkane (2,2,4-trimethylpentane) were found to be less reactive than predicted by SAR. Conversely, the SAR estimates for 2,3-dimethylbutane were approximately 25% lower than the experimental values, with the exception of those estimated by the Wilson group, highlighting the limited understanding of the oxidative 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,$(1.37\pm0.48)\times10^{-11}\exp[-(209\pm100)/T]$, 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 C_3-C_{11} 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., C_5-alkanes emitted from gasoline usage and C_6-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, the alkanes are extremely less reactive with NO_3 and ano reacting with ozone, they are degraded and removed from the atmosphere via gas-phase oxidation reactions with OH radicals and chlorine atoms. (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, degradation products 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).

Numerous laboratories have conducted research on the kinetics of the reaction between alkanes and OH radicals using the absolute rate method and the relative rate method. The absolute rate method (such as flash photolysis and emission flow et al.) 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 method, the relative rate method relies on the recommended rate coefficient 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 coefficient 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 method have been published. For example, Shaw et al. and Phan and Li obtained rate coefficients 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 C_2-C_8 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 C_2-C_6 alkanes, more complex and multifunctional alkanes are often poorly constrained or unmeasured.

Temperature has an important influence on the reaction rate coefficients of alkanes and OH radicals. The reaction rate coefficients 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 coefficients 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 $\geq$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 coefficients 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 coefficients for different types of alkanes at various temperatures.

In this study, the rate coefficients for the reactions of 25 different C_3-C_{11} alkanes with OH radicals were determined using the multivariate relative rate method, including linear alkanes, cycloalkanes, and methyl-alkanes. To validate the rate coefficients 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 coefficients 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

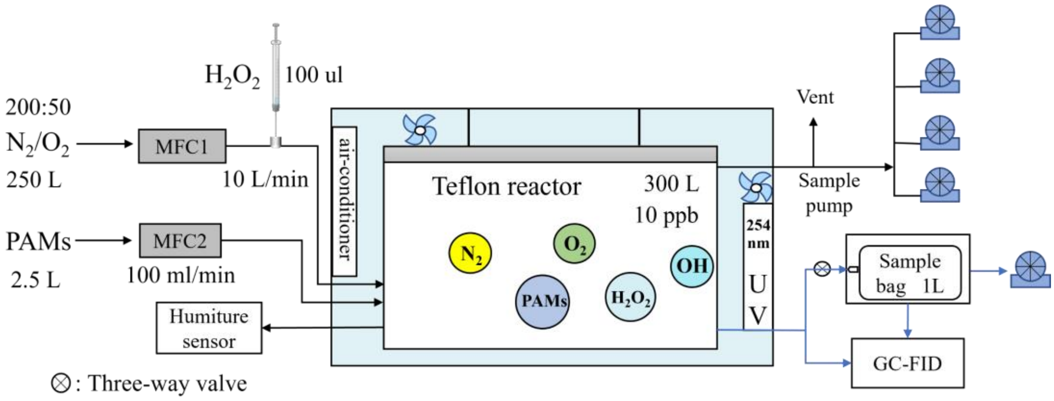

Figure 1. A schematic of the experimental device

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 ± 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 with 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 C_3-C_{11} 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

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

Figure S1(a) reveals that the mixed gas diluted with N_2 underwent a 14-hour reaction in a Teflon reactor without light. The k_d values ranged from 1.3 to 4.8 (the units are $\times10^{-4}$ ppbv/h), implying negligible influence from factors such as alkane loss from reactor walls, self-consumption, or airbag leakage. Figure S1(b) illustrates that the peak height variation for 25 alkanes + 50 μl of H_2O_2 within 15 hours was less than 3%, indicating the insignificance of dark reactions between H_2O_2 and alkanes. When the same concentration mixed gas was irradiated for 7 hours without H_2O_2, alkane concentration changes were depicted in Fig. S2. The results indicated that minimal impact from alkane photolysis on OH radical reaction rate constant determination.

To obtain the reaction rate coefficients of alkanes with OH radicals in 1-2 hour, the alkanes mixture exiting the reactor was collected in more than ten polyvinyl fluoride (PVF) sampling bag (1.0 L) using a transparent vacuum sampling device for GC-FID. Prior to use, the empty sampling bag was flushed with high-purity nitrogen 3 times and placed within the vacuum sampler - a system utilizing an oil-free diaphragm air pump to create a vacuum. The initial concentrations of alkanes sample were collected before the lamp on, and the following sampling process occurred every 10 minutes. Collected samples were subsequently analyzed using a self-developed automated injection system for PVF bag.

2.1.3 Relative rate technique

The rate coefficients were measured by the relative rate method (Atkinson, 1986). The basic principle is that the rate coefficient for the reaction of the reactant used as a reference with OH radicals needs to be the recommended rate coefficients values, rate constant for the reaction of OH radicals with the target compound can be determined by monitoring the simultaneous decay of the target and reference compounds in the presence of OH radicals due to the competitive response mechanism. Additionally, an important criterion for the selection of reference compounds, that is, the reference rate coefficient needs to be similar to the one under study in order to improve sensitivity. To ensure that the reactants only react with OH radicals, the OH radicals need to be in excess in the experiment. The research method of this work is based on the multivariate relative rate method published by Shaw et al. (Shaw et al., 2018), taking the mixed system as the research object, broadening the range of compounds that can be examined.

Taking R (reference compounds) and X (target compounds) as examples, the reaction of OH radicals can be described as follows:

$$R+OH \rightarrow Products\ (k_R) \qquad (R1)$$

$$X+OH \rightarrow Products\ (k_X) \qquad (R2)$$

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

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

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

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

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

Where $[R]_0$ and $[X]_0$ are the concentrations of reference compounds and target compounds before turning on the light; $[R]_t$and $[X]_t$ are the corresponding concentrations after turning on the light for time t. k_R and k_X refer to the second-order rate coefficients for the reaction of the reference compounds and target compounds with OH radicals.

2.1.4 Choice of reference *k* values

It is critical to choose appropriate reference compounds in a kinetics study using the relative rate technique. Some reported values of the rate coefficients for reactions of C_3-C_{11} alkanes with OH radicals have been measured by different methods in different laboratories, and these measurement results may be quite different. When these rate coefficients are measured by the relative rate technique, choosing different reference values will lead to a change of the final experimental target rate constants. In this work, selecting 3 different commonly used reference compounds (n-Hexane, Cyclohexane, n-Octane) to determine the rate coefficients for each reaction at room temperature to check the consistency of kinetic results. The selection of *k* values for reference compounds and the literature data assessment and comparison gives priority to the available expert-evaluated rate coefficients wherever possible. Here we used the recommended expert-evaluated data of database for Version 2.1.0 of McGillen et al. (Database for the Kinetics of the Gas-Phase Atmospheric Reactions of Organic Compounds – Eurochamp Data Center), which is relatively comprehensive and provides rigorously evaluated rate coefficients for many species. Among them, at 298 ± 1 K, the *k* values (in units of cm^3 $molecule^{-1}$ s^{-1}) of the three reference compounds 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 coefficients (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 coefficients 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:

$$k(\mathrm{CH_3\text{-}X})=k^0_{\mathrm{prim}}\mathrm{F}(\mathrm{X})$$

$$k(\mathrm{X\text{-}CH_2\text{-}Y})=k^0_{\mathrm{sec}}\mathrm{F}(\mathrm{X})\mathrm{F}(\mathrm{Y})$$

$$k(\mathrm{X\text{-}CH(Y)Z})=k^0_{\mathrm{tert}}\mathrm{F}(\mathrm{X})\mathrm{F}(\mathrm{Y})\mathrm{F}(\mathrm{Z})$$

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

Where, K_{tot} represents the rate constant of each target compound. k^0_{prim} , k^0_{sec} , k^0_{tert} represent the rate coefficients of each -CH_3, -CH_2- and >CH-. For standard substituent groups such as -CH_3, F(-CH_3)=1.00, X, Y and Z represent substituent groups, F(X), F(Y) and F(Z) refer to the activity coefficient of substituents (X, Y, Z) at different positions on carbon groups. At room temperature, F(-CH_2-)=1.23, F(>CH-)=1.23. Based on an extensive review of kinetic literature values for linear alkanes at room temperature, Atkinson and Kwok et al derived the values of k^0_{prim}, k^0_{sec}, k^0_{tert} at room temperature, $k^0_{\mathrm{prim}}=0.136\times10^{-12}$, $k^0_{\mathrm{sec}}=0.934\times10^{-12}$, $k^0_{\mathrm{tert}}=1.94\times10^{-12}$, the unit is cm^3 $molecule^{-1}$ s^{-1}. After that, many researchers continued to update and modify some parameters based on the method of Atkinson and Kwok (Kwok and Atkinson, 1995), and obtained the new base rate coefficients for different positional groups, some examples include: Neeb, Wilson et al., Jenkin et al., and McGillen et al. (Neeb, 2000; Wilson et al., 2006; Jenkin et al., 2018; Mcgillen et al., 2020).

3. Result and Discussion

3.1 Results from relative rate experiments at 298 K

The rate coefficients for the reactions involving OH radical with C_3-C_{11} alkanes in the mixed system were determined at 298±1 K. The concentration curves of target alkanes and the reference compound (n-Hexane) were plotted in Fig. 2. As shown in Fig. 2, the decay of both target and reference compounds correlated well with eq. (7), and high correlation coefficients (R^2) were observed for most alkanes, exceeding 0.99. Table 1 and Table S2 listed the obtained k_{OH} for C_3-C_{11} alkanes under three bath gases using the related reference compounds. The error bars (1σ) in Table 1 accounted for reference rate constant uncertainty, and experimental parameter uncertainties (pressure, temperature, flow rate, reactant concentration). The results indicated strong agreement (within <15%) between rate coefficients for 25 C_3-C_{11} straight-chain, branched-chain, and cycloalkanes, using different reference compounds. For example, the k_{OH} obtained for propane with n-hexane, cyclohexane and n-octane as the reference compound were $(1.38\pm0.01)\times10^{-12}$, $(1.25\pm0.03)\times10^{-12}$ and $(1.34\pm0.04)\times10^{-12}$ (the units are cm^3 $molecule^{-1}$ s^{-1}), respectively (within 10%). This suggests that reference compound variation minimally affects results, 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 C_3-C_{11} 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 ($R_1CH_2R_2$) 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 C_3-C_{11}, the reaction rate coefficient 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 secondary 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 coefficients 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 increases with the increase of cycle size. By comparing the reaction rate coefficients 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 coefficients of cyclopentane and methylcyclopentane (cyclohexane and methylcyclohexane) that the reaction rate coefficient increases about 2.06×10^{-12} cm^3 $molecule^{-1}$ s^{-1} for cycloalkanes with each increase of methyl.

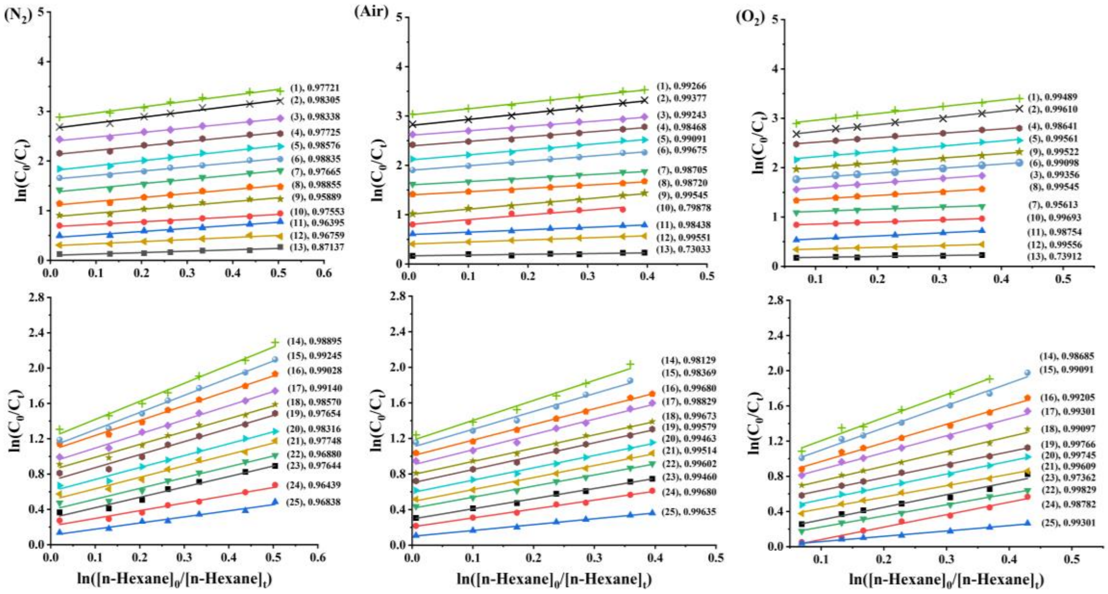

Figure 2. Typical kinetic data as acquired with the multivariate relative rate technique at 298 K and a fixed reaction time of 70 min for the reaction of C_3-C_{11} alkanes with the OH radical using n-hexane as reference compound in different bath gases (N_2, Air, O_2). The numbers in parentheses correspond 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).

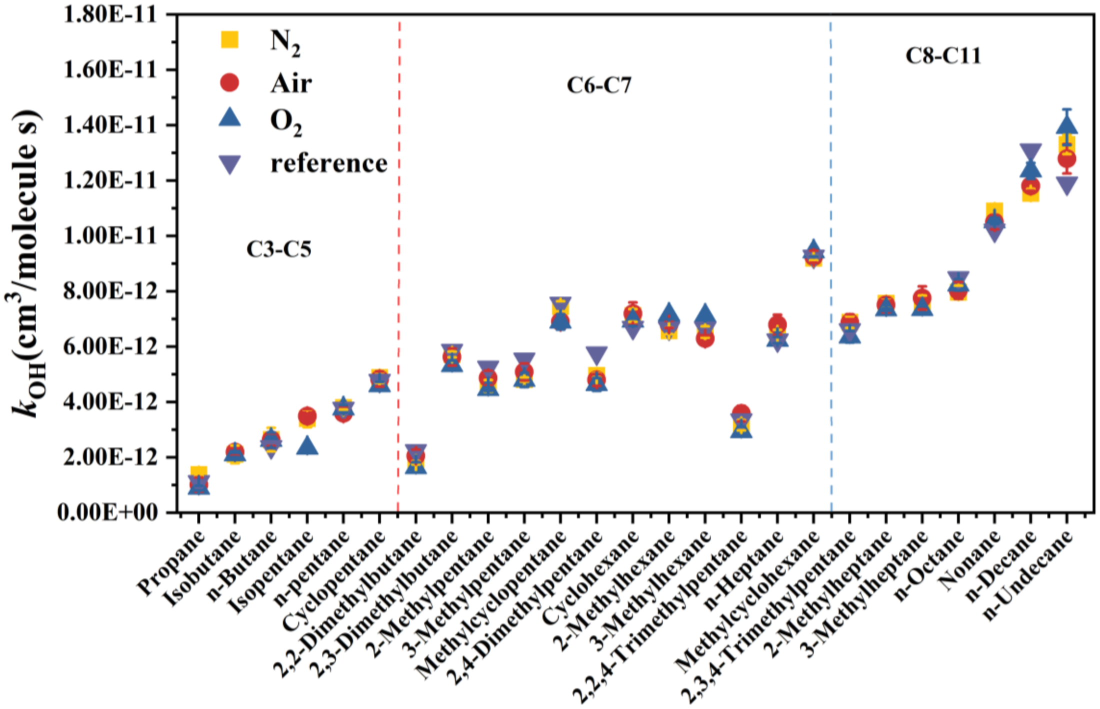

Figure 3. Comparison of rate coefficients of C_3-C_{11} alkanes in different bath gases (N_2, Air, O_2) with expert-evaluated data at 298±1 K. The error bar was taken as 1σ.

The obtained k_{OH} values for C_3-C_{11} alkanes were compared with literature-reported values (Table 1). For several n-alkanes, such as n-butane, the average rate coefficients obtained in 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 coefficients 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 coefficients 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 coefficients 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 (7.14×10^{-12}, 7.19×10^{-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 6.70×10^{-12} and 6.38×10^{-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 6.69×10^{-12} and 6.30×10^{-12} (the unit is $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$), respectively. The rate coefficients 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**			**Literature measurements**
		$k_{\mathrm{OH}}/k_{\mathrm{reference}}$ ±1σ	**k_{OH} ±1σ ($\times10^{-12}$ cm^3 molecule^{-1} s^{-1})**	**$k_{\mathrm{OH\text{-}av}}$[a] ±1σ ($\times10^{-12}$ cm^3 molecule^{-1} s^{-1})**	**k_{OH} ($\times10^{-12}$cm^3 molecule^{-1} s^{-1})**
Propane				(1.01±0.26)	1.11 [bcd]
	n-Hexane	0.190±0.033	(9.43±1.66)		1.09 [e]
	Cyclohexane	0.153±0.028	(1.03±0.18)		1.91 [f]
	n-Octane	0.136±0.031	(1.16±0.26)		(1.15±0.15) [g]
Isobutane	n-Hexane	0.444±0.012	(2.21±0.06)	(2.19±0.13)	2.12 [h]

	Cyclohexane	0.315±0.008	(2.08±0.02)		2.22[i]
	n-Octane	0.264±0.005	(2.24±0.04)		(2.34±0.33)[j]
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[b r]
	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)		
2,3-Dimethylbutane	n-Hexane	1.095±0.061	(5.44±0.31)	(5.62±0.31)	5.78[e] (6.14±0.25)[p] 6.03[h]
	Cyclohexane	0.809±0.039	(5.42±0.26)		
	n-Octane	0.728±0.050	(6.05±0.29)		
2-Methylpentane	n-Hexane	0.972±0.022	(4.83±0.11)	(4.86±0.26)	5.2[e] (5.25±0.25)[p] 5.00[f] 4.75[s]
	Cyclohexane	0.722±0.054	(4.83±0.36)		
	n-Octane	0.625±0.045	(5.30±0.38)		
3-Methylpentane	n-Hexane	1.014±0.030	(5.04±0.15)	(5.08±0.31)	5.20[e] (5.54±0.25)[p] 4.93[s]
	Cyclohexane	0.777±0.059	(5.20±0.40)		
	n-Octane	0.669±0.082	(5.67±0.70)		
methylcyclopentane	n-Hexane	1.432±0.053	(7.12±0.27)	(7.31±0.29)	(7.65±0.10)[u]
	Cyclohexane	1.007±0.023	(6.73±0.15)		(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±0.20)	4.80[e]

	Cyclohexane	0.721±0.046	(4.83±0.31)		5.51[s]
	n-Octane	0.596±0.026	(5.05±0.22)		(5.76±0.40)[p]
Cyclohexane	n-Hexane	1.372±0.054	(6.82±0.27)	(7.20±0.33)	6.97[e] 7.14[q] 6.38[h] 6.70[b] (7.19±0.10)[u] (6.85±0.20)[p]
	Cyclohexane	--	--		
	n-Octane	0.872±0.022	(7.39±0.19)		
2-Methylhexane	n-Hexane	1.369±0.004	(6.80±0.02)	(6.80±0.13)	(6.69±0.10)[u]
	Cyclohexane	0.993±0.022	(6.64±0.15)		
	n-Octane	0.800±0.031	(6.78±0.26)		
3-Methylhexane	n-Hexane	1.266±0.003	(6.29±0.02)	(6.29±0.11)	(6.30±0.10)[u]
	Cyclohexane	0.984±0.046	(6.58±0.31)		
	n-Octane	0.807±0.122	(6.73±0.74)		
2,2,4-Trimethylpentane	n-Hexane	0.702±0.033	(3.49±0.16)	(3.58±0.28)	3.34[e] 3.64[s] (3.34±0.25)[p] (3.71±0.10)[v]
	Cyclohexane	0.557±0.032	(3.72±0.21)		
	n-Octane	0.435±0.065	(3.69±0.55)		
n-Heptane	n-Hexane	1.280±0.066	(6.36±0.33)	(6.78±0.36)	6.76[e] 6.68[y] 6.80[h] (6.70±0.15)[g]
	Cyclohexane	0.961±0.020	(6.43±0.26)		
	n-Octane	0.828±0.029	(7.03±0.25)		
Methylcyclohexane	n-Hexane	1.906±0.098	(9.48±0.49)	(9.25±0.22)	9.60[e] (9.64±0.30)[p] (11.8±1.00)[F] (9.50±0.14)[D] (9.29±0.10)[u]
	Cyclohexane	1.349±0.012	(9.02±0.08)		
	n-Octane	1.160±0.016	(9.83±0.14)		
2,3,4-Trimethylpentane	n-Hexane	1.355±0.050	(6.73±0.25)	(6.87±0.30)	6.60[e] 6.50[h] (6.60±0.26)[p]
	Cyclohexane	1.008±0.039	(6.74±0.26)		
	n-Octane	0.861±0.039	(7.30±0.33)		
2-Methylheptane	n-Hexane	1.532±0.062	(7.62±0.31)	(7.49±0.27)	9.10[L]
	Cyclohexane	1.061±0.029	(7.09±0.19)		
	n-Octane	0.931±0.025	(7.89±0.21)		
3-Methylheptane	n-Hexane	1.532±0.070	(7.62±0.35)	(7.71±0.35)	--
	Cyclohexane	1.055±0.072	(7.06±0.48)		
	n-Octane	0.948±0.036	(8.04±0.31)		
n-Octane	n-Hexane	1.680±0.038	(8.35±0.19)	(8.03±0.32)	8.11[e] 8.42[m] (8.48±0.10)[z]
	Cyclohexane	1.157±0.027	(7.74±0.18)		
	n-Octane	--	--		
Nonane	n-Hexane	2.166±0.079	(10.76±0.39)	(10.50±0.26)	9.70[e] 10.20[A] 10.70[w]
	Cyclohexane	1.449±0.028	(9.69±0.19)		
	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)	(11.81±0.18)	11.00 ^{e}
	Cyclohexane	1.668±0.022	(11.16±0.15)		(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)	(12.78±0.53)	12.30 ^{e}
	Cyclohexane	1.668±0.022	(11.16±0.15)		12.50 ^{B}
	n-Octane	1.588±0.056	(13.50±0.60)		(11.90±2.00) ^{p}

a: Weighted average $k_{av} = (w_{ref1}k_{ref1}+w_{ref2}k_{ref2}+\ldots)/\ (w_{ref1}+w_{ref2}+\ldots)$, where $w_{ref1}=1/\sigma_{ref1}^{2}$, etc. The error, σ_{av}, was given by: $\sigma_{av} = (1/\sigma_{ref1}+1/\sigma_{ref2}+\ldots)^{-0.5}$.

b: (Demore and Bayes, 1999); c: (Mellouki et al., 1994); d: (Talukdar et al., 1994); e: (Atkinson and Arey, 2003); f: (Cox et al., 1980); g: (Morin et al., 2015); h: (Wilson et al., 2006); i: (Tully et al., 1986); j: (Edney et al., 1986); k: (Perry et al., 1976); m: (Greiner, 1970a) ; n: (Donahue et al., 1998); o: (Harris and Kerr, 1988); p: (Calvert et al., 2015); q: (Droege and Tully, 1987); r: (Singh et al., 2013); s: (Badra and Farooq, 2015) u: (Sprengnether et al., 2009); t: (Anderson et al., 2004); v: (Greiner, 1970b), y: (Crawford et al., 2011) ; z: (Li et al., 2006); L: (Shaw et al., 2020); w: (Atkinson et al., 1982); A: (Ferrari et al., 1996); B: (Sivaramakrishnan and Michael, 2009); D: (Bejan et al., 2018); F: (Ballesteros et al., 2015).

3.2 Comparisons to structure-activity relationships

To assess the accuracy of the estimation technique, multiple comparisons were made between the obtained reaction rate coefficients 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 C_3-C_{11} 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 branched 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 area. 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 5%) (Neeb, 2000; Wilson et al., 2006), However, compared with the SAR values of Atkinson and Kwok et al. and Jenkin et al., this result is about 15% and 8% lower. The result suggested that the reaction activity of these cycle-chain alkanes estimated with SAR methods (Kwok and Atkinson, 1995; Jenkin et al., 2018) might be overestimated to varying degrees.

In addition, there are a number of SAR methods that are quite different in their estimation from those of Atkinson, Wilson, et al. and Neeb, et al., for instance, the method of McGillen et al. Figure S3 shows a comparison of our measurements with the SAR estimates of McGillen et al. Similar to the results of Kwok and Atkinson, Neeb, and Jenkin et al., the obtained k_{OH} values of cyclopentane and 2,3-Dimethylbutane in this study exceed the shaded area. This further illustrates that there is still a large discrepancy between the experimental values and the SAR estimates for both substances. For cycloalkanes, the SAR estimates of McGillen et al. are still overestimated to varying degrees compared to our measurements, especially for cyclopentane, where the experimentally measured k_{OH} in this work is still about 34% lower than the SAR estimate. And the k_{OH} values for cyclohexane, methylcyclopentane and methylcyclohexane were also lower than the estimated values by about 18%, 12% and 5%, respectively. For the branched alkanes, again the k_{OH} of 2,3-Dimethylbutane is higher than the SAR estimate by about 32% or so. Similarly to the comparison with the Neeb, and Jenkin et al SAR estimates, the experimental measurements we obtained for 2,2,4-Trimethylpentane are also lower than the McGillen et al estimates by about 14%. By comparing the reaction rate coefficients of cyclopentane and cyclohexane, it is found that for cyclic alkanes of Kwok and Atkinson, Neeb, Jenkin et al., and McGillen et al, the cycle size increases by about1.41×10^{-12} cm^3 $molecule^{-1}$ s^{-1}. However, For the SAR estimate of Wilson et al, the cycle size increases by about 1.12×10^{-12} cm^3 $molecule^{-1}$ s^{-1}.

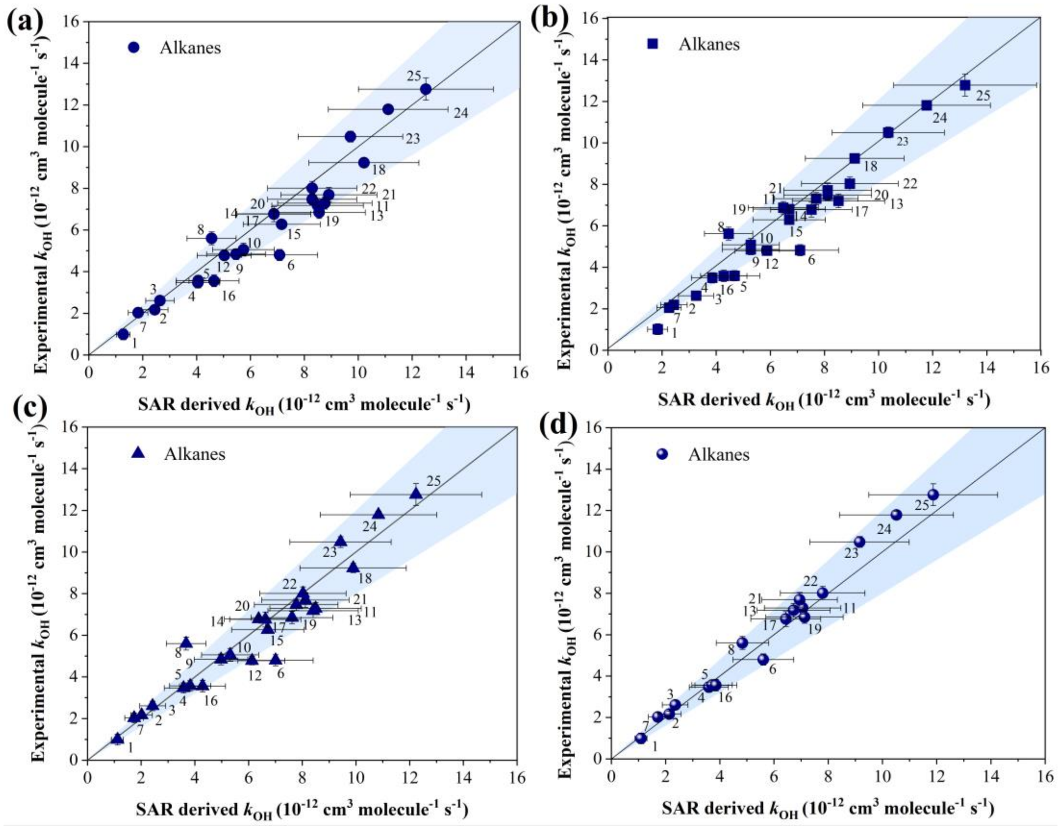

Figure 4. Measured Alkanes + OH rate coefficients plotted against SAR-derived rate coefficients for all compounds (a. (Kwok and Atkinson, 1995); b. (Neeb, 2000); c. (Jenkin et al., 2018); d. (Wilson et al., 2006)). The shaded area demonstrates a 20 % uncertainty in the 1:1 black gradient line. The alkanes 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) n-nonane; (24) n-Decane; (25) n-Undecane.

3.3 Temperature dependence (273-323 K)

In order to investigate the relationship between temperature and reaction rate coefficient, experiments were carried out in this study in the tropospheric temperature range (273-323 K), and the Arrhenius formulas was obtained for this temperature range. Also, our data were 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: $k(T)=(2.43\pm0.52)\times10^{-11}\ \exp\ [-(481.2\pm60)/T]$ 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 coefficient, only the temperature dependence of the reaction rate coefficient under the air system is considered here. Measured values for 24 C_3-C_{10} 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. S4-S16).

Table 2. Summary of Arrhenius Expression of the Reaction of OH radical with C_3-C_{11} alkanes in this work and other studies.

Alkanes	**Temperature (K)**	**A-factor ^{a} ($\times 10^{-11}$)**	**E_a/R^b (K)**	**Technique ^{c}**	**Literature measurements**
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)
	298-416	0.629	126	AR-UV	(Gordon and Mulac, 1975)
n-pentane	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)
	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)
n-Heptane	273-323 *240-1364	3.96±0.37 4.48	544±28 116, n=1.72	RR/DP/GC-FID	this work
	*290-1090	1.73	406, n=2	Review	(Atkinson and Arey, 2003)
	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	4.39	138, n=1.7	AR/DF/LIF	(Morin et al., 2015)
	298-500	0.986	600	Theory	(Cohen, 1991)
	*241-1287 838-1287	6.03 248±17	32, n=1.4 193	AR-UV	(Sivaramakrishnan and Michael, 2009)
	869-1364	243	180	AR-UV	(Pang et al., 2011)
	*240-1364	3.84	148, n=1.79	recommended	(Mcgillen et al., 2020)
n-Octane	273-323 *240-1080	4.22±0.49 3.60	497±34 251, n=1.78	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)
	*290-1080	2.42	361, n=2.00	Review	(Atkinson and Arey, 2003)
	296-497	2.57	332±65	AR/FP/KS	(Greiner, 1970a)
	*298-1000	0.986	600, n=2.2	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)
Isobutane	273-323	2.29±0.74	739±94	RR/DP/GC-FID	this work
	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	273-323	1.12±0.11	443±34	RR/DP/GC-FID	this work
	213-407	1.39±0.12	424±25		
	213-407	1.52	432	RR/DP/GC	(Wilson et al., 2006)
Cyclopentane	273-323	3.67±0.63	619±51	RR/DP/GC-FID	this work
	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)
Cyclohexane	273-323	3.62±0.59	522±48	RR/DP/GC-FID	this work
	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)
Methylcyclopentane	273-323	1.65±0.19	262±33	RR/DP/GC-FID	this work
	*230-1344	1.59	439, n=2.15		
	*230-370	--	--	AR/DF/LIF	(Sprengnether et al., 2009)
	*230-1344	1.67	454, n=2.15		McGillen, 2020
Methylcyclohexane	273-323	4.39±0.58	475±29	RR/DP/GC-FID	this work
	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)
2,2-Dimethylbutane	273-323	3.53±1.28	899±106	RR/DP/GC-FID	this work
	240-330	3.37	809	Review	(Atkinson and Arey, 2003)
	243-328	--	--	RR/DP/GC	(Harris and Kerr, 1988)

	254-1327	6.14±0.90	1023±76	AR/DF/LIF	(Badra and Farooq, 2015)
2,3-Dimethylbutane	273-323 *273-1366	1.15±0.09 1.29	219±24 437, n=2.09	RR/DP/GC-FID	this work
	*240-1220	1.47	407, n=2.00	Review	(Atkinson and Arey, 2003)
	300-498	2.24	321	AR/FP/GC	Greiner,1970
	*250-1366	1.3	427, n=2.08	AR/DF/LIF	(Badra and Farooq, 2015)
	*220-1292	1.6	364, n=1.96	Review	(Sivaramakrishnan and Michael, 2009)
2,4-Dimethylpentane	273-323	2.03±0.17	452±24	RR/DP/GC-FID	this work
	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)
3-Methylpentane	273-323	2.44±0.39	511±17	RR/DP/GC-FID	this work
	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)
2-Methylhexane	273-323 273-385	1.30±0.08 1.82±0.09	222±19 321±16	RR/DP/GC-FID	this work
	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	1.37±0.48	209±100	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)

[a, b]The error bar was taken as σ.

[c]RR: relative rate; AR: absolute rate; DF: discharge flow; DP: direct photolysis; FP: flash photolysis; EB: electron beam; UV: Ultraviolet; GC: gas chromatography; FID: flame ionization detection; LIF: laser induced fluorescence; FTIR: fourier transform infrared spectrometer; MS: mass spectrometry; KS: kinetic-spectroscopy.

* The expression takes the form $k(T) = A*\exp(Ea/RT)*(T/300)^n$

A. OH+ n-Octane. Figure 5 (a) exhibits the Arrhenius plot for the reaction between n-Octane and OH radicals, covering a temperature range of 240 to 1080 K. Within the experimental temperature range (273-323 K), our data align well with previous studies. The derived Arrhenius expression is as follow: $k_{\text{n-Octane}}(T)=(4.22\pm0.49)\times10^{-11}\exp[-(497\pm34)/T]$ (T=273-323 K). The result agree well with the Arrhenius expression of $(4.52\pm0.37)\times10^{-11}\exp[-(538\pm27)/T]$ $cm^3\cdot molecule^{-1}\cdot s^{-1}$ reported by Wilson et al. (Wilson et al., 2006) between 284 and 384 K, but contrast the expressions of $(2.27\pm0.21)\times10^{-11}\exp[-(296\pm27)/T]$ $cm^3\cdot molecule^{-1}\cdot s^{-1}$ reported by Li et al. between 240 and 340 K (Li et al., 2006) and $(2.57)\times10^{-11}\exp[-(332\pm65)/T]$ $cm^3\cdot molecule^{-1}\cdot s^{-1}$ reported by Greiner (Greiner, 1970a) between 296 and 497 K. Fit our data to expert-evaluated data (manually entered data from multiple sources), the derived Arrhenius expression in 240-1080 K is as follow: $k_{\text{n-Octane}}(T)=3.60\times10^{-12}*\exp(251/T)*(T/300)^{1.78}cm^3\ molecule^{-1}\ s^{-1}$. This result is slightly consistent with the recommended expression ($k_{\text{n-Octane}}(T)=2.42\times10^{-12}*\exp(361/T)*(T/300)^{2.00}$ for and Arey (Atkinson and Arey, 2003). By comparison, our data are highly consistent with the data recommended by experts. The obtained Arrhenius expression more accurately represents the relationship between the reaction rate coefficient of octane and OH radicals and temperature in 273-323 K and a wide temperature range, which has certain reference significance. Further investigations are necessary to understand the discrepancies amongst these studies. Also, the experimental values of n-Octane obtained at different temperatures are in high agreement with the SAR estimates.

B. OH+ n-Heptane. The Arrhenius plot in Fig. 5 (b) displays the reaction between n-Heptane and 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. The Arrhenius expression obtained is $k_{\text{n-Heptane}}(T)=(3.96\pm0.38)\times10^{-11}\exp[-(544\pm28)/T]$. This result agrees well with the Arrhenius expression of $(3.38\pm0.17)\times10^{-11}\exp[-(497\pm16)/T]$ $cm^3\cdot molecule^{-1}\cdot s^{-1}$

reported by Wilson et al. (Wilson et al., 2006) between 241 and 406 K. By fitting our data and recommended data from multiple sources to the Arrhenius equation, the resulting Arrhenius expression at 240-1364 K is as follow: $k_{\text{n-Heptane}}(\text{T})=4.48\times10^{-12}*\exp(116/\text{T})*(\text{T}/300)^{1.72}$ cm^3 molecule^{-1} s^{-1}. This result is in good agreement with the expression ($k_{\text{n-Heptane}}(\text{T})=4.39\times10^{-12}*\exp(138/\text{T})*(\text{T}/300)^{1.70}$) obtained by Morin et al (Morin et al., 2015) at 248-896 K. Compared to the recommended data from the database of McGillen et al. (Mcgillen et al., 2020) at 240-1464 K, the finger activation energy obtained in this work is more in line with that of (148), however, the pre-finger factor A obtained (4.48) is about 17% higher than that (3.84).

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 obtained at 273-323 K is $k_{\text{Isopentane}}(\text{T})=(1.12\pm0.11)\times10^{-11}\exp[-(443\pm34)/\text{T}]$. The Arrhenius expression at 213-407 K obtained by fitting our data and those of Wilson et al. is as follows: $k_{\text{Isopentane}}(\text{T})=(1.39\pm0.12)\times10^{-11}\exp[-(424\pm25)/\text{T}]$ cm^3 molecule^{-1} s^{-1}. The results are similar to the relative experimental results of Wilson et al. $(1.52\pm0.21)\times10^{-11}\exp[-(432\pm27)/\text{T}]$ 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). In the temperature range studied (273-323 K), the Arrhenius expression obtained in this work is $k_{\text{2,3-Dimethylbutane}}(\text{T})=(1.15\pm0.09)\times10^{-11}\exp[-(219\pm24)/\text{T}]$ cm^3 molecule^{-1} s^{-1}. Linear regression applied to our data and high temperature data in the literature (at 273-1366 K) yields the Arrhenius expression as follows: $k_{\text{2,3-Dimethylbutane}}(\text{T})=1.29\times10^{-12}*\exp(437/\text{T})*(\text{T}/300)^{2.09}$ cm^3 molecule^{-1} s^{-1}. This result agrees well with the Arrhenius expression of $k_{\text{2,3-Dimethylbutane}}(\text{T})=1.30\times10^{-12}*\exp(427/\text{T})*(\text{T}/300)^{2.08}$ cm$^3\cdot$molecule$^{-1}\cdot$s^{-1}

at 250-1366 K reported by Badra and Farooq (Badra and Farooq, 2015).

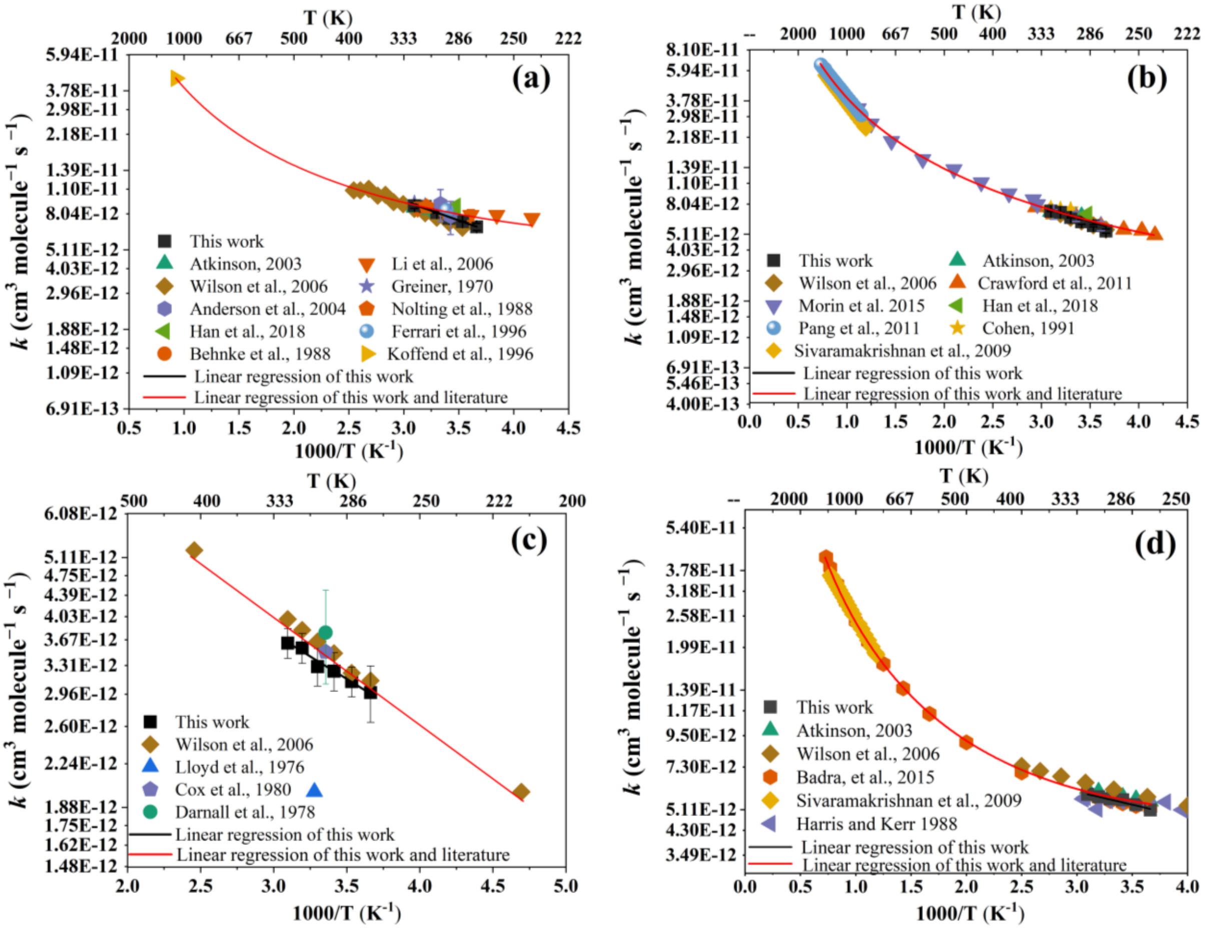

Figure 5. Arrhenius plots for the reaction of n-Octane (a), n-Heptane (b), Isopentane (c) and 2,3-Dimethylbutane (d) with OH radical in wide temperature range along with available literature data. The error bar was taken as 2σ.

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. The rate coefficients of methylcyclopentane at 273-323 K in this work were obtained. 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. Fitting our data at 273-323 K yields the Arrhenius expression of $k_{\text{Methylcyclopentane}}(T) = (1.65\pm0.19)\times10^{-11}\exp[-(262\pm33)/T]$. Additionally, they derived an alternative Arrhenius expression to accommodate the curved behavior of the rate constant between 230 and 370 K, making it difficult to directly compare with our Arrhenius expression. Besides, in order to obtain temperature-dependent relationships over a wide temperature range, 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: $k_{\text{Methylcyclopentane}}(T) = 1.59\times10^{-12}*\exp(439/T)*(T/300)^{2.15}$ cm^3 molecule^{-1} s^{-1}. The result is highly consistent with the expert-evaluated Arrhenius expression of methylcyclopentane ($k_{\text{Methylcyclopentane}}(T) = 1.67\times10^{-12}*\exp(454/T)*(T/300)^{2.15}$ cm^3 molecule^{-1} s^{-1}), indicating that the data obtained has a certain degree of reliability. Fitting our data at 273-323 K yields the Arrhenius expression of $k_{\text{2-Methylhexane}}(T) = (1.30\pm0.08)\times10^{-11}\exp[-(222\pm19)/T]$. At present, the research on the temperature dependence of 2-Methylhexane only includes the measured reaction rate coefficient with OH radical of Sprengnether et al. by absolute rate technique at 230-385 K. The Arrhenius expression obtained by fitting our data with Sprengnether et al's data at 230-385 K is as follows: $k_{\text{2-Methylhexane}}(T) = (1.82\pm0.09)\times10^{-11}\exp[-(321\pm16)/T]$ cm^3 molecule^{-1} s^{-1}. Expert-evaluated Arrhenius expression is $k_{\text{2-Methylhexane}}(T) = (1.21\pm0.07)\times10^{-11}\exp[-(171\pm16)/T]$ cm^3 molecule^{-1} s^{-1}. Through comparison, it can be clearly seen that the two are consistent, indicating that the obtained Arrhenius expression has certain reference value. To the best of our knowledge, this is the first investigation of the temperature-dependent kinetics for the reaction of methylcyclopentane and 2-methylhexane with OH radicals utilizing the relative rate technique.

F. OH+ 3-Methylheptane. In Figure 6 (c), the Arrhenius plot presents the reaction between 3-Methylheptane and OH radicals, spanning a temperature range of 273 to 323 K. A linear regression analysis of our data yields the following Arrhenius expressions: $k_{\text{3-Methylheptane}}(T) = (2.72\pm0.34)\times10^{-11}\exp[-(456\pm28)/T]$ cm$^3\cdot$molecule$^{-1}\cdot$s^{-1}. We believe this study to be the first investigation of the temperature-dependent kinetics for the reaction between 3-Methylheptane and OH radicals. The only previous study on this reaction, reported by Shaw et al. (Shaw et al., 2020) utilizing the relative rate method in nitrogen at 323 K, demonstrates significantly higher data (>65%) compared to our results. Possible explanations for this discrepancy lie in the different reference compounds used and potential sample loss during sampling in the enrichment tube in Shaw et al.

G. OH+ 3-Methylhexane (Figure 6 (d)). This is the first temperature-dependence relative data. It can be seen from the figure that this data is this data is significantly lower by approximately 80%

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

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

H. OH+ 2-Methylheptane (Figure 6 (e)). There are no previous temperature dependence data on this compound. Similar to 3-Methylhexane, this data is lower by approximately 37% compared to Shaw et al. at room temperature. Within the range of 273-323 K, the obtained Arrhenius expression is as follows:

$k_{\text{2-Methylheptane}}(T) = (1.37\pm0.48)\times10^{-11}\exp[-(209\pm100)/T]$ cm^3 molecule^{-1} s^{-1}.

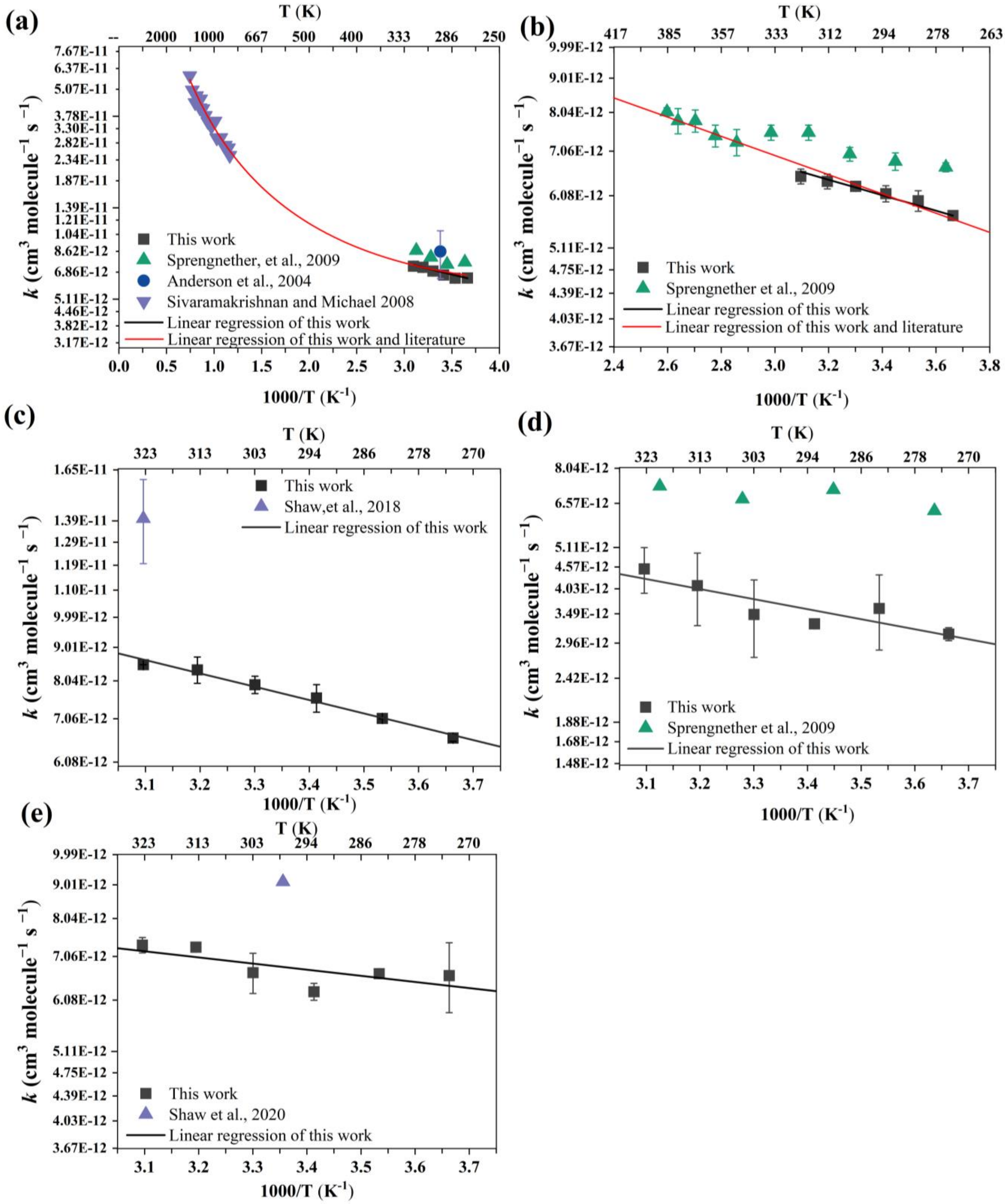

Figure 6. Arrhenius plots for the reaction of Methylcyclopentane (a), 2-Methylhexane (b), 3-Methylheptane (c), 3-Methylhexane (d) and 2-Methylheptane (e) with OH radical along with available literature data. The error bar was taken as 2σ.

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 C_3-C_{11} 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 weak, 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 $\log_{10}[k_{(Cl+alkanes)}] = 0.521\times\log_{10}[k_{(OH+alkanes)}]-3.670$ 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. It is currently known that the rate coefficient for the reaction of 2,2,3-trimethylpentane with OH radical at room temperature is 4.84×10^{-12} cm^3 molecule^{-1} s^{-1}, according to the above correlation equation, it can be inferred that the rate coefficient with Cl atoms is 2.72×10^{-10} cm^3 molecule^{-1} s^{-1}.

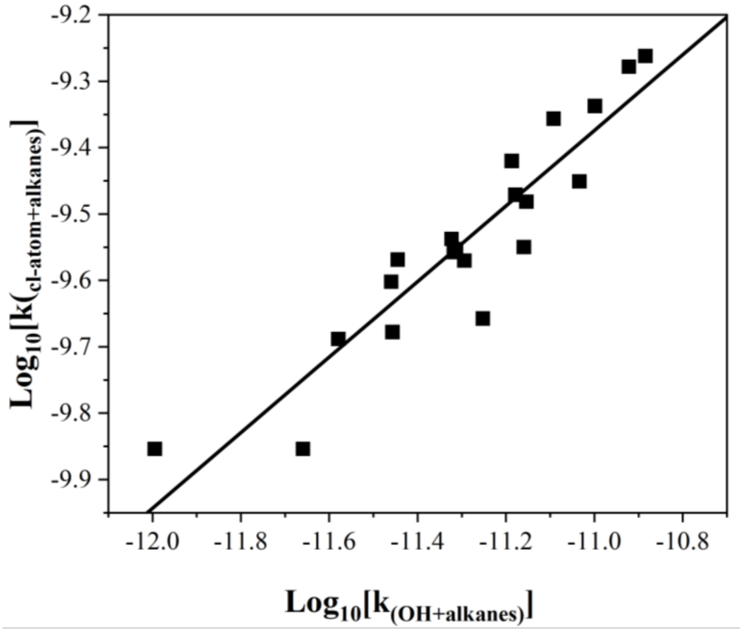

Figure 7. Double logarithmic plot ($\log_{10}$) of the rate coefficients for the reaction of Cl-atoms versus the reaction of OH radicals with the saturated alkanes (C_3-C_{11} alkanes studied above). The solid line represents the unweighted least-squares fit to the data.

3.5 Atmospheric lifetime and implications

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

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

Where τ_{alkane} is the atmospheric lifetime of the alkane due to OH removal, $k_{\text{alkane+OH}}$ is the rate coefficient 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 1×10^{6} molecules cm^{-3} (Lawrence et al., 2001). Using the $k_{\text{alkane+OH}}$ (298 K) values determined in the present work, the atmospheric lifetime for 25 alkanes was estimated and listed in Table S4. As can be seen from the table, the atmospheric lifetimes of C_3-C_{11} alkanes reacting with OH radicals are about 1-11 days. As the carbon chain grows, the atmospheric lifetimes are reduced, 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. Alkyl peroxyl radicals will serve to convert NO to NO_2 directly, leading to the production of tropospheric ozone. Longer atmospheric residence time of short-chain alkanes compared to long-chain C_8-C_{11} alkanes, such as propane, the lifetime is 11 days.

4. Conclusions

The use of the multivariate relative rate method in this study allowed for the simultaneous determination of reaction rate coefficients of C_3-C_{11} alkanes and OH radicals, which significantly improved the efficiency of determination. A total of 25 relative rate coefficients at room temperature were obtained, including the determination of a previously unreported room temperature relative rate coefficient for 3-methylheptane. For the studied n-alkanes, the obtained rate coefficients (k_{OH}) were found to be consistent with results estimated by the SAR methods using parameters provided by various positional groups, such as Atkinson and Kwok, Neeb, Wilson, Jenkin, and McGillen. However, it is important to note that parameters other than those provided by Wilson group do not appear to reasonably estimate the rate coefficients of 2,3-dimethylbutane. Additionally, SAR estimates for several cyclic alkanes (cyclopentane, methylcyclopentane, cyclohexane) and branched alkanes (2,2,4-trimethylpentane) appear to be overestimated compared to our measurements. This raises reasonable suspicion that these methods may still lack consideration of additional factors. Arrhenius expressions for the reaction of 2-Methylhepane and 3-Methylheptane with OH radicals were obtained for the first time in the temperature range of 273-323 K, expanding the existing database. In addition, correlation equations for the rate coefficients of alkanes reacting with OH radicals and chlorine atoms were obtained, and the rate coefficient of 2,2,3-trimethylpentane with chlorine atoms, which has not yet been reported, was deduced. The atmospheric lifetimes of the alkanes were also obtained for further prediction of their environmental impact.

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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