

Reply to Reviewer's Comments

RC3: Major comments:

1. The introduction provides a large number of literature data; however, a very chaotic presentation induces to readers the feeling of jumping from one study to another, all of them mostly with very general information regarding the kinetic of alkanes. The studies mentioned in the introduction are presented without an effective detail of the rate coefficient information. I would write the introduction assessing the importance of alkanes for air quality with their impact to atmosphere, then I would add information about their concentrations in troposphere and the impact on potential ozone formation, potential SOA formation and their sources and sinks. One important point of the study is to highlight the importance of accurate kinetic rate coefficients for database, global model atmospheric processes and degradation mechanisms. As one of the reviewers mentioned already, the McGillen et al., (2018) database is very important to be used as a start in the literature data assessment and comparison.

Reply: Thanks for your valuable suggestions! The introduction section has been modified in the revised manuscript based on your suggestions.

... 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 NO₃ radicals, Cl atoms and ozone (O₃) (Atkinson and Arey, 2003; Shi et al., 2019). These oxidation processes will form a photochemical smog in the presence of NO_x 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)....

.... 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)...

2. The reason of selected those 25 alkanes is not presented in the study and their selection looks arbitrary. An organized evaluation based on their separation on straight-chain, branching and cyclic alkane structure would be more interesting and helpful to get valuable information. First class of alkanes including linear compounds could provide information regarding reactivity of each CH₂ group added to their structure and how the rate coefficient value would change over increasing alkane chain. Secondly, from the branching alkanes the authors could have more information related to CH groups added to the alkane structure. The third class in the evaluation would be cyclic alkanes where the authors could extract information regarding the reactivity increase with the cycle size from cyclobutane to cyclodecane. The authors should include in their evaluation the alkanes rate coefficients studied in present study and those existing in the literature, to release more complete discussion on their behaviour and reactivity (figure 3 and 4). As an example, there are a lot of data which could be included, mentioning here only a few (k_{OH} for cyclooctane, bicyclo octane, methyl octane, etc.).

Reply: Thanks for your valuable suggestions! The 25 selected alkanes are the alkanes in the PAMs mixed gas that are widely present in the atmospheric environment and contribute significantly to O₃ production. The classification discussion of 25 alkanes has been added in the revised manuscript based on your suggestions.

...For each additional CH₂ group from C₃-C₁₁, the reaction rate constant increases about 0.95-1.81 (the unit is 10⁻¹² cm³ 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 CH₂ group reaction rate increases by about 2.37 × 10⁻¹² cm³ 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 cm³ molecule⁻¹ s⁻¹ for cycloalkanes with each increase of methyl.

3. Since the authors highlight their first study on 3-methylheptane why they do not cover other not studied yet branched alkanes (2,2,3-trimethylpentane, etc.)

Reply: This work mainly focuses on the study of 25 kinds of alkanes in PAMs mixed gases, which are widely present in the atmospheric environment and contribute significantly to the production of O₃. However, 2,2,3-trimethylpentane is not included in the PAMs mixed gases. The reaction rate constant of 2,2,3-trimethylpentane with OH radical can be further measured in our future studies.

4. The data reported in the Table 2 should be reevaluated and presented in more concise and understandable form. There are multiple examples of inconsistency of the data with many average data not well calculated (i.e. isopentane in N₂).

Reply: Sorry for the mistake! The data reported in the Table 2 had been reevaluated and presented in more concise and understandable form in the revised manuscript.

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 ($\times 10^{-11}$)	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)
	273-323	3.78±0.66	867±52	RR/DP/GC-FID	this work
n-Butane	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)
	240-896	5.06±0.45	602±30	RR/DP/GC-FID	this work
n-Heptane	290-1090	1.28±0.21	190	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	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
n-Octane	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	1.78	235	Review	(Atkinson and Arey, 2003)
	296-497	2.57	332±65	AR/FP/KS	(Greiner, 1970)
	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, 1970)
	220-407	1.02±0.03	463±10	RR/DF/MS	(Wilson et al., 2006)
Isopentane	273-323	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
	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)
Cyclopentane	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)
Methylcyclopentane	230-1344	7.21±0.38	705±28	RR/DP/GC-FID	this work
	230-1344	6.81±0.39	641±38	AR/DF/LIF	(Sprenghether 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	(Sprenghether et al., 2009)
	273-323	3.53±1.28	899±106	RR/DP/GC-FID	this work
2,2-Dimethylbutane	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)
	253-323	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)
	273-323	2.53±1.45	575±161	RR/DP/GC-FID	this work
3-Methylhexane	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
	273-323	1.61±0.22	499±40	RR/DP/GC-FID	this work
2,2,4-Trimethylpentane	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)
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)

^{a, b}The error bar was taken as σ .

^cRR: 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.

5. With the extensive interpretation of data including the existing literature rate coefficients, the authors would be able to evaluate the accurate reactivity trends for the class of alkane toward OH radicals and calculate new factors for the SAR method and then to improve the SAR method. A simple comparison with the Kwok and Atkinson SAR method is not worth to do. Evaluation of existing SAR approaches in the literature, with discussion about the influence on the substituent factors, is necessary. (McGillen et al., 2024 (doi.org/10.1039/D3EA00147D), Jenkin et al., 2018 (doi.org/10.5194/acp18-9297-2018)).

Reply: Thanks for your valuable suggestions! Only the alkane data of this work had been classified and discussed to evaluate the reactivity trends of alkanes towards OH radicals in the revised manuscript.

...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 (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...

...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...

6. The reaction channel of the OH radical initiated degradation of alkanes is strictly related to hydrogen abstraction in the presence of oxygen. There are clearly correlations on the alkane reactivity with OH radicals and Cl atoms for all saturated class of VOCs. Please evaluate a log-log correlation of k_{Cl} and k_{OH} as presented by Calvert et al., 2011 (Calvert, J., Mellouki, A., Orlando, J., Pilling, M., and Wallington, T.: Mechanisms of Atmospheric Oxidation of the Oxygenates, Oxford University Press) for alkanes, saturated alcohols and ethers and also by Tovar et al. (2022) (doi.org/10.5194/acp-22-6989-2022) for saturated epoxides.

Reply: Thanks for your valuable suggestions! More discussion on correlation between the rate coefficients of the reaction of alkanes with OH radicals and chlorine atoms had been added in our revised manuscript.

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 $\log_{10}[k_{(Cl+alkanes)}] = 0.521 \times \log_{10}[k_{(OH+alkanes)}] - 3.670$ 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...

7. The importance of the bath-gas is over highlighted in this study and a single example for a selected alkane would be enough to prove that is no bath-gas effect on the rate coefficient value. A revaluation of the paper consistency should be performed.

Reply: Thanks for your valuable suggestions! As you and other reviewer mentioned, there is always some small amount of O₂ in the N₂ bath gas, the impact of bath gas has been reduced in our revised manuscript. For example, the study on relative rate experiments and temperature dependence in different bath gases in Section 3.1 and 3.3 have been removed, with the discussion now centered on the temperature dependence relationship in the air system.

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

The rate constants for the reactions involving OH radical with C3-C11 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 S4 listed the obtained k_{OH} for C3-C11 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 constants for 25 C3-C11 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 $(1.38 \pm 0.01) \times 10^{-12}$, $(1.25 \pm 0.03) \times 10^{-12}$ and $(1.34 \pm 0.04) \times 10^{-12}$ (the units are $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), 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 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...

...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: $k(T) = (2.43 \pm 0.52) \times 10^{-11} \exp[-(481.2 \pm 60)/T]$ 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...

...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. Fit our data to expert-evaluated data (manually entered data from multiple sources), the derived Arrhenius expressions are as follows: $k_{n-Octane}(T) = (5.07 \pm 0.97) \times 10^{-11} \exp[-(543 \pm 61)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This result agree well with the Arrhenius expression of $(4.52 \pm 0.37) \times 10^{-11} \exp[-(538 \pm 27)/T] \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ reported by Wilson et al. (Wilson et al., 2006) between 284 and 384

K and $(4.95 \pm 0.87) \times 10^{-11} \exp [-(531 \pm 56)/T]$ recommended Arrhenius formula obtained by experts' evaluation of data processing, but contrast the expressions of $(2.27 \pm 0.21) \times 10^{-11} \exp [-(296 \pm 27)/T]$ $\text{cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ reported by Li et al. between 240 and 340 K (Li et al., 2006) and $(2.57) \times 10^{-11} \exp [-(332 \pm 65)/T]$ $\text{cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ reported by Greiner (Greiner, 1970) between 296 and 497 K. 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 constant of octane and OH radicals and temperature in a wide temperature range, which has certain reference significance....

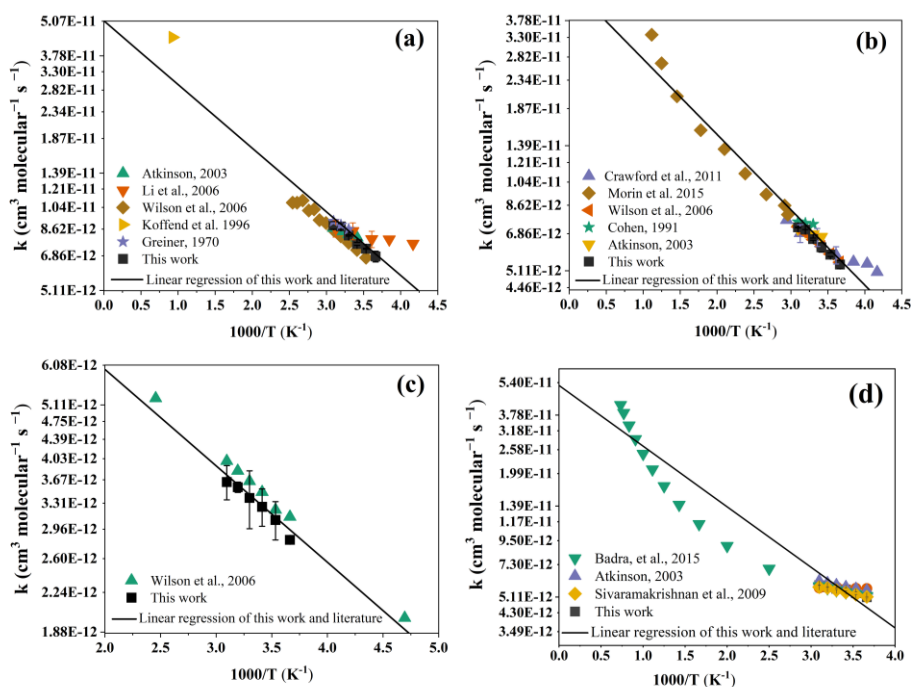


Figure 5. Arrhenius plots for the reaction of n-Octane (a), n-Heptane (b), Isopentane (c) and 2,3-Dimethylbutane (d) with OH radical in wide temperature range along with available literature data. The error bar was taken as 2σ .

8. Please add more information regarding the conditions needed for relative rate techniques. Also include more advantages and disadvantages of the absolute and relative techniques.

Reply: Thanks for your valuable suggestions! More information regarding the conditions needed for relative rate techniques and more advantages and disadvantages

of the absolute and relative techniques in this work in the introduction section had been added in our revised manuscript.

...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)...

9. The authors should highlight the atmospheric implication and the impact of their research as requested by a scientific journal as “Atmospheric Chemistry and Physics”. Please add information about the alkane lifetime in the atmosphere toward the OH radicals. A more extensive conclusion and atmospheric implication should be performed.

Reply: Thanks for your valuable suggestions! The atmospheric lifetime and implications had been added in the in the revised manuscript.

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

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

where τ_{alkane} is the atmospheric lifetime of the alkane due to OH removal, $k_{\text{alkane}+\text{OH}}$ is the rate constant for the reaction of the alkane with OH radical at the typical tropospheric temperature of 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} (Li et al., 2018). Using the $k_{\text{alkane}+\text{OH}}$ (298 K) values determined in the present work, the atmospheric lifetime for 25 alkanes was estimated and listed on the Table S3. 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 O₂ in the atmosphere. The subsequent reaction of alkyl peroxy radicals enhances the conversion of NO to NO₂ by HO₂ 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...

Minor comments:

Line 84: Finlayson-Pitts

Reply: Thanks for your valuable suggestions! Modifications have been made in the literature in the revised manuscript.

Finlayson-pitts, B. J., Hernandez, S. K., and Berko, H. N.: A new dark source of the gaseous hydroxyl radical for relative rate measurements, *Journal of Physical Chemistry*, 97, 1172-1177, 10.1021/j100108a012, 1993.

Line 127: “at253”

Reply: Thanks for your valuable suggestions! Modifications have been made in the revised manuscript.

...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...

Line 130: please avoid given values in the form of 0.00013 or 0.00048. Change the units to pptv/h.

Reply: Thanks for your valuable suggestions! The form of 0.00013 or 0.00048 had been revised in the revised manuscript.

...The K_d values ranged from 1.3 to 4.8 (the units are 10⁻⁴ ppbv/h)...

Line 283 and 285: please add units

Reply: Sorry for the mistake! Units have been added in the revised manuscript.

... in the air gas is (2.63±0.23), the unit is 10⁻¹² cm³ molecule⁻¹ s⁻¹ (applicable to all units involved in this paragraph).

Line 460: please revise the rate coefficient

Reply: Yes! The rate coefficient had been revised in the revised manuscript.

...Linear regression applied to our data and expert- recommended data (at 253-263 K) yields the Arrhenius expression as follows:

$k_{2,3\text{-Dimethylbutane}}(T) = (4.81 \pm 0.56) \times 10^{-12} \exp [-(669 \pm 50)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \dots$

Line 104: The figure of the simulation chamber shows a ratio of 200:50 of N₂:O₂ mixture. The study used synthetic air or this mixture shown in the figure?

Reply: Thank you for your question. As shown by the figure of the simulation chamber, the air used in this study is a mixture of nitrogen (200L) and oxygen (50L) at 4:1.

References

- 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, 10.1021/cr00071a004, 1986.
- Atkinson, R.: Atmospheric chemistry of VOCs and NO_x, *Atmos. Environ.*, 34, 2063-2101, 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, 10.5194/acp-3-2233-2003, 2003.
- Atkinson, R. and Arey, J.: Atmospheric degradation of volatile organic compounds, *Chem. Rev.*, 103, 4605-4638, 10.1021/cr0206420, 2003.
- 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.
- 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, *International Journal of Chemical Kinetics*, 50, 544-555, 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 Cl₂, CH₄, and C₃H₈, *J. Phys. Chem. A*, 108, 10464-10472, 10.1021/jp047340h, 2004.
- Cohen, N.: Are reaction rate coefficients additive? Revised transition state theory calculations for OH + alkane reactions, *International Journal of Chemical Kinetics*, 23, 397-417, <https://doi.org/10.1002/kin.550230506>, 1991.
- 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, *International Journal of Chemical Kinetics*, 43, 489-497, <https://doi.org/10.1002/kin.20574>, 2011.
- DeMore, W. and Bayes, K.: Rate constants for the reactions of hydroxyl radical with several alkanes, cycloalkanes, and dimethyl ether, *The Journal of Physical Chemistry A*, 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, *The Journal of Physical Chemistry A*, 102, 3121-3126, 1998.
- Droege, A. T. and Tully, F. P.: Hydrogen-atom abstraction from alkanes by hydroxyl radical. 6. cyclopentane and cyclohexane, *Journal of Physical Chemistry*, 91, 1222-1225, 1987.
- 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, 10.1029/2004jd005485, 2005.
- Gordon, S. and Mulac, W.: Reaction of the OH ($X \cdot 71'$) radical produced by the pulse radiolysis of water vapor *Int. J. Chem. Kinet.*, (Syrnp. 1), 289, 299, 1975.
- Greiner, N. R.: Hydroxyl Radical Kinetics by Kinetic Spectroscopy. VI. Reactions with Alkanes in the Range 300–500°K, *J. Chem. Phys.*, 53, 1070-&, 10.1063/1.1674099, 1970.
- Guenther, A.: The contribution of reactive carbon emissions from vegetation to the carbon balance of terrestrial ecosystems, *Chemosphere*, 49, 837-844, 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, *International Journal of Chemical Kinetics*, 20, 939-955, 10.1002/kin.550201203, 1988.
- 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, 10.1021/jp0638134, 2006.
- 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, 10.1016/j.envsci.2013.12.004, 2014.
- 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, *International Journal of Chemical Kinetics*, 47, 629-637, <https://doi.org/10.1002/kin.20936>, 2015.
- 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, 10.1063/1.432167, 1976.
- 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, *Atmospheric Chemistry and Physics*, 18, 4039-4054, 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, *Atmospheric Environment*, 207, 75-81, 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 C₅-C₈ Cycloalkanes at 240-340 K using the Relative Rate/Discharge Flow/Mass Spectrometry Technique, *J. Phys. Chem. A*, 117, 10863-10872, 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, 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, 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, *Atmospheric Environment*, 141, 560-570, 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, *International Journal of Chemical Kinetics*, 26, 973-990, 10.1002/kin.550261003, 1994.
- 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, 3593-3604, 10.1021/jp055841c, 2006.