

Reply to Reviewer's Comments

RC1: Major reply:

1. The authors assessment of the kinetics literature is currently incomplete. This is made clear by the fact that they take credit for making the first temperature-dependent measurements in cases where measurements are clearly available, as well as the incomplete literature data presented in Table 2. I would suggest that the authors make use of the database paper of McGillen et al. (2020), and download the accompanying database. This will achieve two things: 1. It will give the authors a more comprehensive knowledge of the kinetics literature for OH + hydrocarbon reactions. 2. It will provide these authors with critically evaluated rate coefficients for many of the species that are contained within their paper. Regarding the latter, I would strongly encourage the authors to use these recommendations as their reference rate constants where applicable and reanalyze their data accordingly, and if not, I would expect the authors to justify why they do not accept these recommendations.

Reply: Thanks for your valuable suggestions! As your suggestion, we looked at the study reported by McGillen et al. (2020) and used the accompanying version 2.1.0 database, specifically the reference rate constants using the data recommended by this database and the selection part of the k value had been revised in Section 2.1.4 in the revised manuscript.

... The selection of k values for reference compounds and the literature data assessment and comparison gives priority to the available expert-evaluated rate constants 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 $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) of the three reference compounds selected respectively are expert-evaluated rate constants: $k_{\text{OH}+n\text{-Hexane}}=4.97 \times 10^{-12}$, $k_{\text{OH}+\text{Cyclohexane}}=6.69 \times 10^{-12}$, $k_{\text{OH}+n\text{-Octane}}=8.48 \times 10^{-12}$, 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. At the same time, we updated the data in Table 1 accordingly and reanalyzed our data, such as Section 3.1.

Sec.3.1...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%).....

In addition, a comparison of all species with the recommended reaction rate constants of the database has been added (Figure 3) and discussed.

As shown in Fig. 3, for the different bath gases, the obtained k_{OH} for C3-C11 alkanes showed high agreement. Meanwhile, it can also be observed from the figure that most of the rate coefficients obtained are very similar to the expert-evaluated values of the database by the McGillen et al. However, 2,4-Dimethylpentane is an exception, the k_{OH} value obtained in this study is about 20% lower than the recommended value, but it is similar to expert-evaluated value by Atkinson and Arey (Atkinson and Arey, 2003). Additionally, it can be clearly seen in the figure that the reactivity of linear alkanes (RCH_2R) with OH radicals increasing...

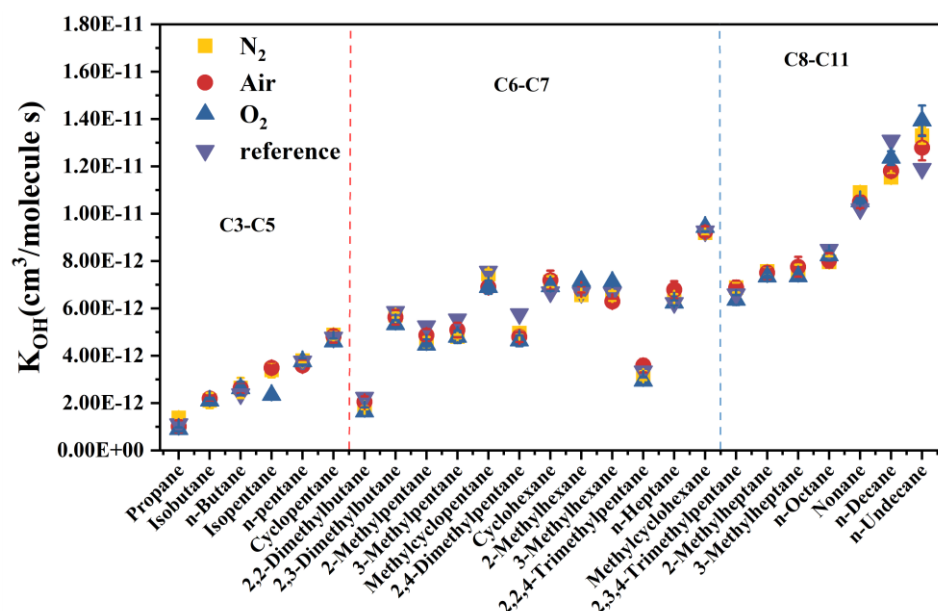


Figure 3. Comparison of rate constants of C3-C11 alkanes in different bath gases (N_2 , Air, O_2) with expert-evaluated data at 298 ± 1 K. The error bar was taken as 1σ .

2. The presentation of the data/ quality of the data is unsatisfactory. When I inspect the contents of Table 1, taking the reference rate constants as provided on page 7 of the manuscript, I am able to reproduce k_{OH} for the first 3 entries (i.e. propane in N₂ with n-hexane, cyclohexane and n-octane as references). Following this, the next 3 entries (propane in air) are inconsistent. I noticed that throughout this table there are many problems of this type. In my judgement, this is not acceptable for a paper whose principle subject is kinetic data and it undermines your experimental work. What is the purpose of this data, if your readers cannot trust it? For this reason, I insist that the authors return to their spreadsheets, remake this table correctly and triple check its contents.

Reply: Sorry for the mistake! According to your valuable suggestions, the rate constants recommended by McGillen et al., (2020) database have been used, and the Table 1 has been corrected in the revised manuscript.

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

Alkanes	Reference	This work		Reference
		$k_{OH}/k_{reference}$ ±1σ	k_{OH} ±1σ (×10 ⁻¹² cm ³ molecule ⁻¹ s ⁻¹)	k_{OH-av} ^a ±1σ (×10 ⁻¹² cm ³ molecule ⁻¹ s ⁻¹)
Propane	n-Hexane	0.190±0.033	(9.43±1.66)	1.11 ^{bcd} 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)	2.12 ^h 2.22 ⁱ
	Cyclohexane	0.315±0.008	(2.08±0.02)	(2.19±0.13)
	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)	(2.36±0.25) ^b
	Cyclohexane	0.398±0.017	(2.66±0.12)	(2.72±0.27) ^k

	n-Octane	0.345±0.042	(2.93±0.36)		(2.56±0.25) ^m (2.46±0.15) ^d
Isopentane	n-Hexane	0.684±0.033	(3.40±0.17)	(3.49±0.25)	3.60 ^e
	Cyclohexane	0.512±0.026	(3.43±0.18)		3.65 ^h
	n-Octane	0.442±0.025	(3.75±0.22)		3.50 ^f
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
	Cyclohexane	0.527±0.021	(3.53±0.14)		(3.97±0.20) ^p
	n-Octane	0.454±0.029	(3.85±0.24)		(4.20±0.15) ^g
Cyclopentane	n-Hexane	0.951±0.033	(4.72±0.17)	(4.82±0.27)	4.97 ^e 4.83 ^b 5.02 ^q
	Cyclohexane	0.711±0.043	(4.76±0.29)		(4.90±0.20) ^p
	n-Octane	0.600±0.029	(5.09±0.24)		4.84 ^{br}
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
	Cyclohexane	0.722±0.054	(4.83±0.36)		4.75 ^s
	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 (8.60±0.30) ^p (8.60±2.20) ^t
	Cyclohexane	1.007±0.023	(6.73±0.15)		
	n-Octane	0.849±0.017	(7.00±0.24)		
2,4-Dimethylpentane	n-Hexane	0.962±0.012	(4.78±0.06)	(4.80±0.20)	4.80 ^e 5.51 ^s (5.76±0.40) ^p
	Cyclohexane	0.721±0.046	(4.83±0.31)		
	n-Octane	0.596±0.026	(5.05±0.22)		

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

	n-Octane	1.287±0.017	(10.92±0.14)		10.70 ^w (11.30±1.10) ^z
n-Decane	n-Hexane	2.371±0.073	(11.78±0.36)		11.00 ^e
	Cyclohexane	1.668±0.022	(11.16±0.15)	(11.81±0.18)	(12.9±1.00) ^z
	n-Octane	1.401±0.006	(11.88±0.05)		
n-Undecane	n-Hexane	2.371±0.073	(11.78±0.36)		12.30 ^e
	Cyclohexane	1.668±0.022	(11.16±0.15)	(12.78±0.53)	12.50 ^B
	n-Octane	1.588±0.056	(13.50±0.60)		(11.90±2.00) ^P

a: Weighted average $k_{av} = (w_{ref1} k_{ref1} + w_{ref2} k_{ref2} + \dots) / (w_{ref1} + w_{ref2} + \dots)$, where

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

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. The authors insistence on Arrhenius parameters for this selection of reactions in Section 3.3. is unjustified. With all the high-temperature data available for this collection of compounds, it is plainly obvious that the Arrhenius equation is insufficient to describe the temperature dependencies of any of these reactions. The only reason for using such an equation would be for datasets spanning a small temperature range (or where data precision is insufficient). I strongly encourage the authors to consider fitting their data within the context of the available measurements, because I don't think these new Arrhenius parameters add any value to your paper.

Reply: Thanks for your valuable suggestions! Fitting our data to wide temperature range data from the literature for the 9 alkanes discussed in detail in the article. Detailed

description has been added in Section 3.3. in the revised manuscript.

...**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, 1970a) 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. Further investigations are necessary to understand the discrepancies amongst these studies.

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. By fitting our data and recommended data from multiple sources to the Arrhenius equation, the resulting Arrhenius expressions are as follows: $k_{n-Heptane}(T)=(5.06\pm 0.45)\times 10^{-11}\exp[-(602\pm 30)/T]\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$. This result agree well with the Arrhenius expression of $(5.20\pm 0.54)\times 10^{-11}\exp[-(605\pm 39)/T]\text{ cm}^3\cdot\text{molecule}^{-1}\cdot\text{s}^{-1}$ reported by Morin et al. (Morin et al., 2015) between 248 and 896 K. The recommended Arrhenius equation for the reaction of OH radical and n-Heptane is in the form $k(T)=3.84\times 10^{-12}\cdot\exp(148/T)$

* $(T/300)^{1.79}$. Rearrange the fitting data to get the Arrhenius expression in the form of $k(T) = (4.82 \pm 0.43) \times 10^{-11} \exp [-(600 \pm 31)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Compared with the Arrhenius expression recommended in the literature, the preexponential factor A (5.01 ± 0.42) of this work is agree well with the one (4.82 ± 0.43) of recommended (the unit is $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). However, the activation energy E_a/R of this work is about 60% higher than the recommended data.

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

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

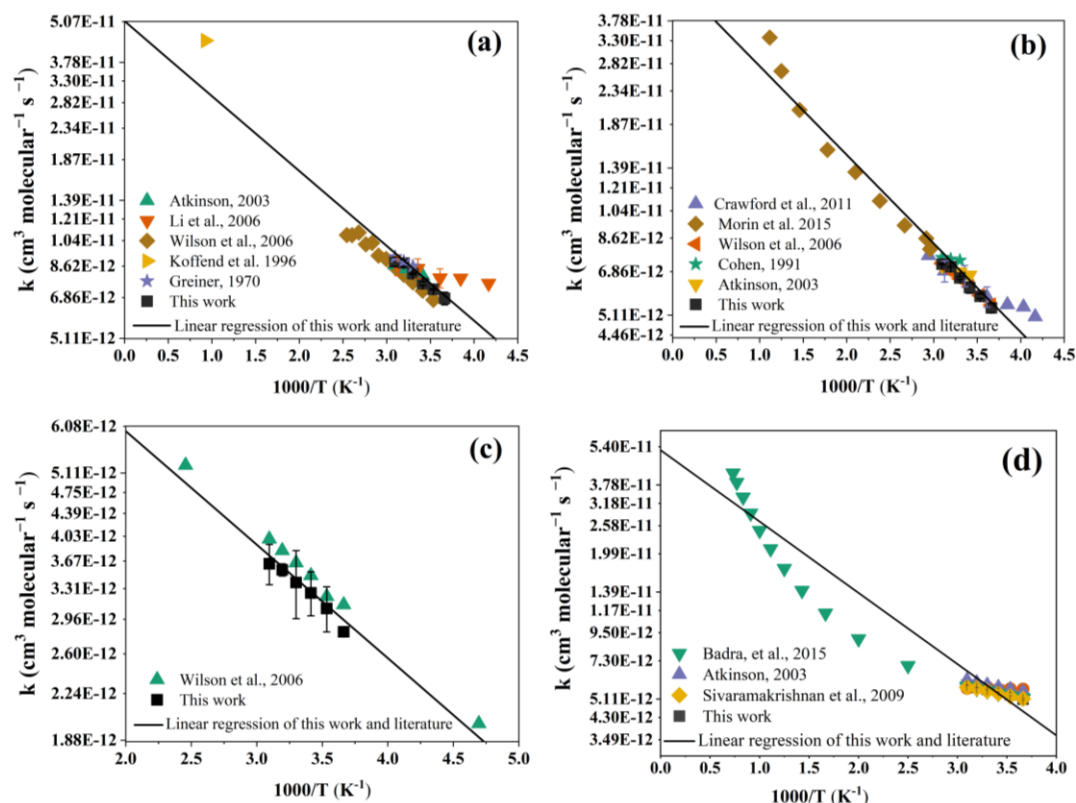


Figure 5. Arrhenius plots for the reaction of n-Octane (a), n-Heptane (b), Isopentane (c) and 2,3-Dimethylbutane (d) with OH radical in wide temperature range along with available literature data. The error bar was taken as 2σ .

4. Problems with general consistency. This is an example (but there are several others), Figure 6(a) shows temperature-dependent literature measurements for OH + methylcyclopentane. In the abstract, it states that “... Arrhenius expressions (in units of $\text{cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$) for the reactions of various cyclo- and branched alkanes with OH were determined for the first time: methylcyclopentane...”. I can interpret this in one of two ways: 1. The authors don’t appear to be aware that there is temperature-dependent data, even though they have presented it in their figures. 2. The authors are discounting the work of Sprengnether et al. because it is not presented in Arrhenius form. If the former, then the authors should organize their manuscript more carefully. If the latter, then I find this to be a strange idea (after all, if you don’t like their equation, just re-fit their data with an Arrhenius equation!)

Reply: Thanks for your valuable suggestions! We are very sorry that we did not consider the different forms of temperature dependence expressions to fit the original data to obtain the same Arrhenius equation as ours. Table 2 has been updated 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)
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)
n-pentane	298-420	1.76	559	AR/ DF/RF	(Perry et al., 1976)
	298-416	0.629	126	AR-UV	(Gordon and Mulac, 1975)
	273-323	0.90±0.05	310±17	RR/DP/GC-FID	this work
	233-364	1.94	494	RR/DP/GC	(Demore and Bayes, 1999)
	300-390	2.97	608	AR/EB/LIF	(Donahue et al., 1998)
n-Heptane	224-372	2.45±0.21	516±25	AR/FP/LIF	(Talukdar et al., 1994)
	243-325	--	--	RR/DP/GC	(Harris and Kerr, 1988)
	240-896	5.06±0.45	602±30	RR/DP/GC-FID	this work

	290-1090	1.28±0.21	190	Review	(Atkinson and Arey, 2003)
	241-406	3.38±0.17	497±16	RR/DF/MS	(Wilson et al., 2006)
	240-340	2.25±0.14	293±37	RR/DF/MS	(Crawford et al., 2011)
	248-896	5.2±0.54	605±39	AR/DF/LIF	(Morin et al., 2015)
	298-500	0.0986	600	Theory	(Cohen, 1991)
	240-1080	5.07±0.97	543±61	RR/DP/GC-FID	this work
	240-340	2.27±0.21	296±27	RR/DF/MS	(Li et al., 2006)
	284-384	4.52±0.37	538±27	RR/DF/MS	(Wilson et al., 2006)
n-Octane	290-1080	1.78	235	Review	(Atkinson and Arey, 2003)
	296-497	2.57	332±65	AR/FP/KS	(Greiner, 1970a)
	298-1000	0.0986	600	Theory	(Cohen, 1991)
Nonane	273-323	5.29±0.63	520±35	RR/DP/GC-FID	this work
	240-340	4.35±0.49	411±32	RR/DF/MS	(Li et al., 2006)
n-Decane	273-323	5.78±0.49	499±25	RR/DP/GC-FID	this work
	240-340	2.26±0.28	160±36	RR/DF/MS	(Li et al., 2006)
	273-323	2.29±0.74	739±94	RR/DP/GC-FID	this work
	300-390	0.626	321	AR/EB/LIF	(Donahue et al., 1998)
Isobutane	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	1.39±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)
	230-1344	7.21±0.38	705±28	RR/DP/GC-FID	this work
Methylcyclopentane	230-1344	6.81±0.39	641±38	AR/DF/LIF	(Sprengnether et al., 2009)

	273-323	4.39±0.58	475±29	RR/DP/GC-FID	this work
Methylcyclohexane	273-343	1.85±0.27	195±20	RR/DP/FTIR	(Bejan et al., 2018)
	230-379	1.46±0.07	125±14	AR/ DF/LIF	(Sprengnether et al., 2009)
	273-323	3.53±1.28	899±106	RR/DP/GC-FID	this work
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
2,3-Dimethylbutane	240-1220	3.98±0.41	579±50	Review	(Atkinson and Arey, 2003)
	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)
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	273-385	1.82±0.09	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	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)
	273-323	1.34±0.07	203±15	RR/DP/GC-FID	this work

2,3,4- Trimethylpentane	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 1σ .

^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. It is not clear to me why the authors chose to consider the bath-gas as an important aspect of these measurements. The literature has many examples of measurements that were conducted in a wide variety of bath gases (helium, argon, nitrogen, air etc.). As far as I am aware, no dependence on bath gas has been noted. In fact, a small amount of oxygen would be necessary in relative rate experiments such as yours, otherwise alkyl radicals formed from the hydrogen abstraction reaction would themselves abstract hydrogen from other alkanes in the system, reforming the original alkane, consuming some of the other hydrocarbons and confusing your results. In practice, it is difficult to remove oxygen to such an extent, and I would therefore assume that your experiments are not affected by this anoxic chemistry. Either way, I suggest that bath gas is an irrelevance in this paper and can be ignored.

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, 1970a) 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....

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6. There are some advantages to studying so many compounds simultaneously, the main one being that it can save you some time. However, there are also some possible problems. The main one would be the formation of products which could interfere with some of your analyte peaks. I see no discussion of any sort regarding products of the reaction. Do you see any product peaks in the GC-FID? If not, why not?

Reply: Yes. In our experiments, we used the GC-FID developed by the research team to accurately detect 57 compounds. The advantage of this instrument is that it can easily and quickly observe the attenuation of multiple compounds in less than 1 h. The results of the chromatogram for various species during 10-60 minutes of reaction shows the variation of acetone. For the asymmetrical peak shape of this compound in the GC-FID with OV-1 column, it is difficult to accurately quantified. In the future, we want to study those compounds by the developed GC-FID equipment with polar column.

Minor comments:

General: the symbol for rate constant in the kinetics literature is an italicized lower-case *k*. It is not to be confused with an upper-case **K** (which is reserved for units of kelvin), or an italicized upper-case **K** (which is normally reserved for equilibrium constants).

Reply: Sorry for the mistake! All rate constant symbols **K** and **K_{OH}** have been modified to *k* or *k_{OH}* in the revised manuscript.

For example: Table 1 listed the obtained k_{OH} for C3-C11 alkanes...

...the obtained k_{OH} values all fall within the shadow range.

...

Abstract: revise according to suggestions above.

Reply: Thanks for your valuable suggestions! The Abstract had been revised according to suggestions above in the revised manuscript.

Abstract: Rate coefficients for the reactions of OH radicals with C3-C11 alkanes were determined using the multivariate relative rate technique. A total of 25 relative rate coefficients at room temperature and 24 Arrhenius expressions-in different temperature range were obtained. Notably, a new room temperature relative rate constant for 3-methylheptane that had not been previously reported was determined, and the obtained k_{OH} values (in units of $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) was 7.71 ± 0.35 . Interestingly, whilst results for n-alkanes agreed well with available structure activity relationship (SAR) calculations, the three cyclo-alkanes and one trimethylpentane were found to be less reactive than predicted by SAR. Conversely, the SAR estimate for 2,3-dimethylbutane were approximately 25% lower than the experimental value, highlighting that the limited understanding of the oxidation chemistry of these compounds. Arrhenius expressions (in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for the reactions of various branched alkanes with OH radical were determined for the first time: 2-methylheptane, $(1.62 \pm 0.37) \times 10^{-11} \exp [-(265 \pm 70)/T]$, and 3-methylheptane, $(3.54 \pm 0.45) \times 10^{-11} \exp [-(374 \pm 49)/T]$. 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.

Introduction:

Line 44. why are you making comparisons with NO_3 ? It is well known that the

abstraction reactions are unimportant for the alkanes. Chlorine on the other hand may become important in some environments.

Reply: Thanks for your valuable suggestions! Following your suggestions and those of other reviewers, the discussion involving NO₃ chemistry has been removed from the revised manuscript.

Line 44. “Dehydrogenation” of alkanes leads to alkenes. You mean to say “hydrogen abstraction”.

Line 46. I assume by “rate constants”, the authors mean “room temperature rate constants”. You should specify this.

Line 47. Assuming that the authors have by now become more familiar with the kinetic database, you will of course know that the range of reactivity of alkanes goes from 6.36E-15 (methane) to 2.16E-11 (n-hexadecane) at the time of writing. The range provided is therefore misleading.

Line 47. “mol” is absolutely not an abbreviation of “molecule”. “mol” is an abbreviation of “mole”, which would be highly misleading.

Line 48. Rate constants are not faster or slower than other rate constants. They are larger or smaller.

Reply: Sorry for the mistakes! These mistakes have been corrected in the revised manuscript.

Line 66. In fact, precise measurements are highly desirable in the relative rate method. Low precision in your GC-FID measurements would lead to scatter in your relative rate plots. Therefore, this statement is misleading.

Reply: Thanks for your valuable suggestions! The contents of relative rate method had been revised according to your suggestions and those of several other reviewers, so the description here no longer exists in the revised manuscript.

However, due to its high experimental difficulty, sensitivity to reaction conditions, and high requirements for instrumentation and equipment, the experimental conditions need to be strictly controlled and the measurement is more complicated. Alternatively, the

relative rate method, and this approach is also widely used to determine k_{OH} values for organic compounds. The basic principle is that the rate constant for the reaction of the reactant used as a reference with OH radicals is known, and the reference reaction rate coefficient needs to be similar to the one under study, to increase measurement sensitivity...

Methods:

General comment: several tests have been made with respect to dark losses, photolytic losses etc. However, as far as I can tell, no tests were performed regarding storage in the 1 litre sample bags. In your experiments, your samples are stored for some time before they are analysed by the GC-FID are they not? During this time, your samples are subjected to conditions of higher surface area to volume ratios, and it is here, where I would expect to see the most wall loss.

Reply: Yes! The VOCs loss caused by the storage of samples in PVF bags had been evaluated in our previous work. As shown in Fig.R1, there is no obvious loss of 25 alkanes in the PVF bag for 10 hours.

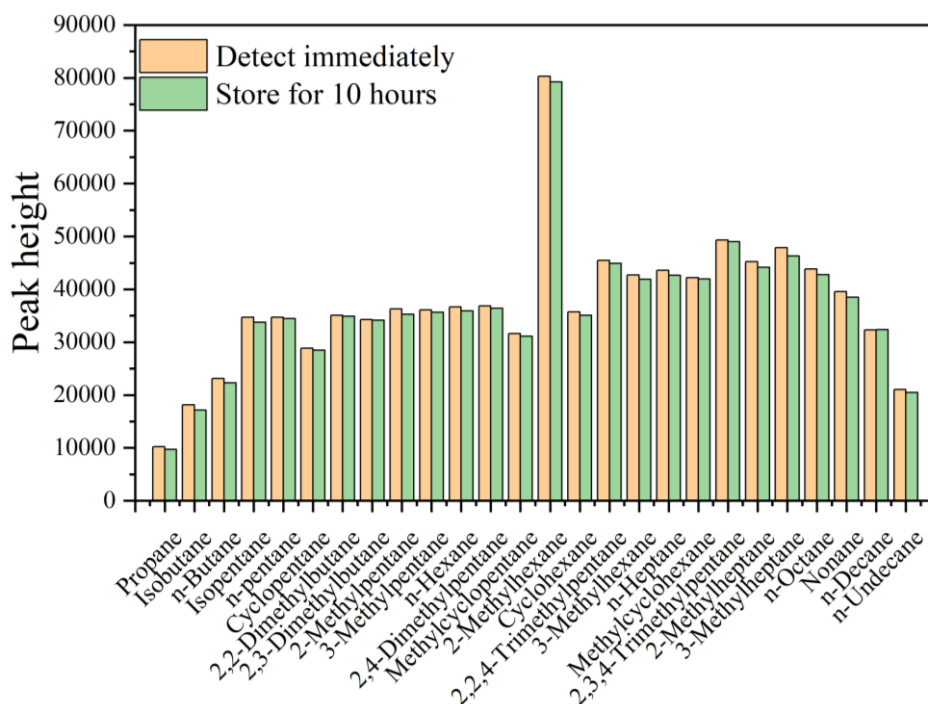


Fig.R1 The VOC loss in PVF bags

Line 115. Excess with respect to what?

Reply: Thank you very much professor for your question! Excess with respect to what has been added in the revised manuscript.

While excess H₂O₂ 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.

Line 145. “self-developed”.

Reply: Sorry for the mistake! The “self-develop” has been modified to “self-developed” in the revised manuscript.

...Collected samples were subsequently analyzed using a self-developed automated injection system ...

Line 155. It is not clear to me how you have improved or expanded the work of Shaw et al. Furthermore, it is also not clear to me how the results of this work are significantly different from any other relative rate study in which several reference compounds are considered.

Reply: Sorry for the mistake! We have corrected it in the revised manuscript. In addition, as you said, there have been many reports on the relative rates of alkanes and OH radicals, but most of them focus on one or several alkanes for experiments. And some data are controversial, the reaction rate constant of 2,4-Dimethylpentane with OH radical evaluated by Atkinson and Arey is $4.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, while the recommended expert-evaluated data of database for Version 2.1.0 of McGillen et al. is $5.76 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is about 20% higher than the data of Atkinson and Arey. The special feature of this work is to select the alkanes in the mixed gas of PAMs, which has an important effect on O₃, and to study it in Shaw et al. Based on the application of multivariate relative rate method, and combined with the GC-FID developed by the experimental group, a large number of compounds can be studied at the same time, and the determination efficiency is improved. In addition, there is still

only one or no reported data for some alkanes, such as 3-methylheptane, which is measured for the first time, making up for the gap in the database.

The research method of this work is based on the multivariate relative rate method published by Shaw et al. (Shaw et al., 2018).

Line 173. There is a certain irony to this statement, because I would strongly recommend that you should use the available expert-evaluated rate constants wherever possible.

Reply: Thanks for your valuable suggestions! The selection of k values for reference compounds has been modified in the revised manuscript.

...The selection of k values for reference compounds and the literature data assessment and comparison gives priority to the available expert-evaluated rate constants 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 $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) of the three reference compounds selected respectively are expert-evaluated rate constants: $k_{\text{OH}+n\text{-Hexane}}=4.97 \times 10^{-12}$, $k_{\text{OH}+\text{Cyclohexane}}=6.69 \times 10^{-12}$, $k_{\text{OH}+n\text{-Octane}}=8.48 \times 10^{-12}$, which is fitted or manually entered data from multiple sources...

Line 193. Was the H₂O₂ purified?

Reply: Yes! H₂O₂ was obtained from Sinopharm Chemical Reagent Co., Ltd. as 30 wt % solution and was concentrated by bubbling helium through it prior to use.

Lines 211-212. I don't know what the authors mean by general error is 2 sigma... Do you mean that the uncertainties for SAR estimates are generally within a factor of two? This is possibly true in a global sense, but it is considerably lower for the alkane dataset (the subject of this paper).

Reply: Thanks for your valuable suggestion! As you mentioned, the 2σ was widely used in the uncertainties analysis for SAR estimates. For the relatively high carbon number of alkanes studied in this study, this value was chosen for comparison with others.

Line 238. I don't know what an "error strip" is. I think the authors mean "error bars".

Reply: Yes. The expression of "error strip" has been replaced with "error bars" in the revised manuscript.

...The error bars (1σ) in Table 1 accounted for data...

Line 238. What is fitting dispersion?

Reply: Reply: Sorry for the mistake! The "fitting dispersion" has been corrected in the revised manuscript.

Results:

Figure 3. It would be useful to include literature recommendations for each of these rate constants where available, allowing us to see how well the experiments are performing.

Reply: Thanks for your valuable suggestions. Comparison with the data of literature recommendations in figure 3 have been added in the revised manuscript.

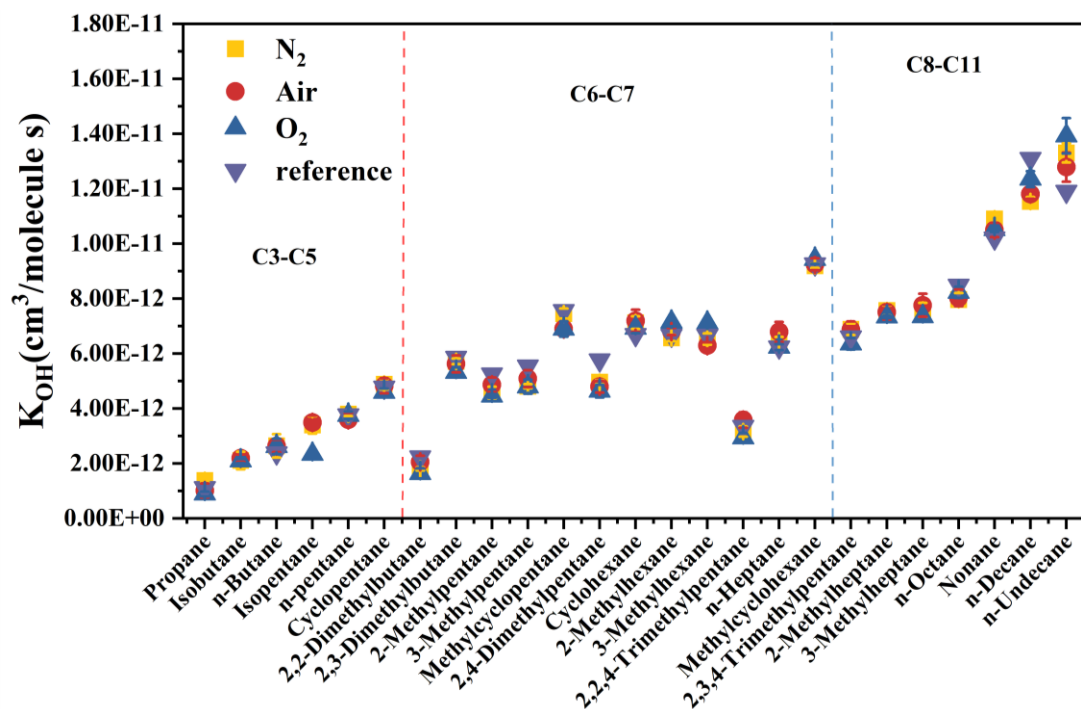


Figure 3. Comparison of rate constants of C3-C11 alkanes in different bath gases (N_2 , Air, O_2) with expert-evaluated data at 298 ± 1 K. The error bar was taken as σ .

Table 1. As noted above, the errors in this table are unacceptable at present. In addition to this, the formatting of this table is confusing and should be rethought to help the readers understand it better.

Reply: We apologize for the error in Table 1 presentation and the error analysis in the manuscript. We have now utilized the rate constants recommended by the McGillen et al., (2020) database as reference rate constants to accurately recreate the table and have meticulously reviewed its content.

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

Alkanes	Reference	This work			Reference
		$k_{OH}/k_{reference} \pm 1\sigma$	$k_{OH} \pm 1\sigma$ ($\times 10^{-12} \text{ cm}^3$ $\text{molecule}^{-1} \text{ s}^{-1}$)	$k_{OH-av}^a \pm 1\sigma$ ($\times 10^{-12} \text{ cm}^3$ $\text{molecule}^{-1} \text{ s}^{-1}$)	k_{OH} ($\times 10^{-12} \text{ cm}^3$ $\text{molecule}^{-1} \text{ s}^{-1}$)
Propane	n-Hexane	0.190 ± 0.033	(9.43 ± 1.66)	(1.01 ± 0.26)	1.11^{bcd}

	Cyclohexane	0.153±0.028	(1.03±0.18)		1.09 ^e
	n-Octane	0.136±0.031	(1.16±0.26)		1.91 ^f (1.15±0.15) ^g
Isobutane	n-Hexane	0.444±0.012	(2.21±0.06)		2.12 ^h 2.22 ⁱ
	Cyclohexane	0.315±0.008	(2.08±0.02)	(2.19±0.13)	(2.34±0.33) ^j
	n-Octane	0.264±0.005	(2.24±0.04)		(2.36±0.25) ^b (2.72±0.27) ^k
n-Butane	n-Hexane	0.516±0.025	(2.56±0.12)		(2.56±0.25) ^m
	Cyclohexane	0.398±0.017	(2.66±0.12)	(2.63±0.23)	(2.46±0.15) ^d
	n-Octane	0.345±0.042	(2.93±0.36)		
Isopentane	n-Hexane	0.684±0.033	(3.40±0.17)		3.60 ^e 3.65 ^h
	Cyclohexane	0.512±0.026	(3.43±0.18)	(3.49±0.25)	3.50 ^f
	n-Octane	0.442±0.025	(3.75±0.22)		
n-pentane	n-Hexane	0.709±0.042	(3.52±0.21)		3.80 ^e 3.98 ⁿ
	Cyclohexane	0.527±0.021	(3.53±0.14)	(3.59±0.25)	4.03 ^o (3.97±0.20) ^p
	n-Octane	0.454±0.029	(3.85±0.24)		(4.20±0.15) ^g
Cyclopentane	n-Hexane	0.951±0.033	(4.72±0.17)		4.97 ^e 4.83 ^b
	Cyclohexane	0.711±0.043	(4.76±0.29)	(4.82±0.27)	5.02 ^q (4.90±0.20) ^p
	n-Octane	0.600±0.029	(5.09±0.24)		4.84 ^{br}
2,2-Dimethylbutane	n-Hexane	0.409±0.019	(2.03±0.09)		(2.23±0.15) ^p 2.15 ^s
	Cyclohexane	0.301±0.030	(2.02±0.20)	(2.05±0.23)	2.32 ^o
	n-Octane	0.264±0.031	(2.24±0.26)		
2,3-Dimethylbutane	n-Hexane	1.095±0.061	(5.44±0.31)		5.78 ^e (6.14±0.25) ^p
	Cyclohexane	0.809±0.039	(5.42±0.26)	(5.62±0.31)	6.03 ^h
	n-Octane	0.728±0.050	(6.05±0.29)		
2-Methylpentane	n-Hexane	0.972±0.022	(4.83±0.11)		5.2 ^e (5.25±0.25) ^p
	Cyclohexane	0.722±0.054	(4.83±0.36)	(4.86±0.26)	5.00 ^f
	n-Octane	0.625±0.045	(5.30±0.38)		4.75 ^s
3-Methylpentane	n-Hexane	1.014±0.030	(5.04±0.15)	(5.08±0.31)	5.20 ^e

	Cyclohexane	0.777±0.059	(5.20±0.40)		(5.54±0.25) ^P
	n-Octane	0.669±0.082	(5.67±0.70)		4.93 ^s
methylcyclopentane	n-Hexane	1.432±0.053	(7.12±0.27)		(7.65±0.10) ^u
	Cyclohexane	1.007±0.023	(6.73±0.15)	(7.31±0.29)	(8.60±0.30) ^P
	n-Octane	0.849±0.017	(7.00±0.24)		(8.60±2.20) ^t
2,4-Dimethylpentane	n-Hexane	0.962±0.012	(4.78±0.06)		4.80 ^e
	Cyclohexane	0.721±0.046	(4.83±0.31)	(4.80±0.20)	5.51 ^s
	n-Octane	0.596±0.026	(5.05±0.22)		(5.76±0.40) ^P
Cyclohexane	n-Hexane	1.372±0.054	(6.82±0.27)		6.97 ^e
	Cyclohexane	--	--	(7.20±0.33)	7.14 ^q
	n-Octane	0.872±0.022	(7.39±0.19)		6.38 ^h
					6.70 ^b
					(7.19±0.10) ^u
					(6.85±0.20) ^P
2-Methylhexane	n-Hexane	1.369±0.004	(6.80±0.02)		
	Cyclohexane	0.993±0.022	(6.64±0.15)	(6.80±0.13)	(6.69±0.10) ^u
	n-Octane	0.800±0.031	(6.78±0.26)		
3-Methylhexane	n-Hexane	1.266±0.003	(6.29±0.02)		
	Cyclohexane	0.984±0.046	(6.58±0.31)	(6.29±0.11)	(6.30±0.10) ^u
	n-Octane	0.807±0.122	(6.73±0.74)		
2,2,4-Trimethylpentane	n-Hexane	0.702±0.033	(3.49±0.16)		3.34 ^e
	Cyclohexane	0.557±0.032	(3.72±0.21)	(3.58±0.28)	3.64 ^s
	n-Octane	0.435±0.065	(3.69±0.55)		(3.34±0.25) ^P
					(3.71±0.10) ^v
n-Heptane	n-Hexane	1.280±0.066	(6.36±0.33)		6.76 ^e
	Cyclohexane	0.961±0.020	(6.43±0.26)	(6.78±0.36)	6.68 ^y
	n-Octane	0.828±0.029	(7.03±0.25)		6.80 ^h
					(6.70±0.15) ^g
Methylcyclohexane	n-Hexane	1.906±0.098	(9.48±0.49)		9.60 ^e
	Cyclohexane	1.349±0.012	(9.02±0.08)	(9.25±0.22)	(9.64±0.30) ^P
	n-Octane	1.160±0.016	(9.83±0.14)		(11.8±1.00) ^F
					(9.50±0.14) ^D
					(9.29±0.10) ^u
2,3,4-Trimethylpentane	n-Hexane	1.355±0.050	(6.73±0.25)		6.60 ^e
	Cyclohexane	1.008±0.039	(6.74±0.26)	(6.87±0.30)	6.50 ^h
	n-Octane	0.861±0.039	(7.30±0.33)		(6.60±0.26) ^P
2-Methylheptane	n-Hexane	1.532±0.062	(7.62±0.31)		
	Cyclohexane	1.061±0.029	(7.09±0.19)	(7.49±0.27)	9.10 ^L

	n-Octane	0.931±0.025	(7.89±0.21)		
	n-Hexane	1.532±0.070	(7.62±0.35)		
3-Methylheptane	Cyclohexane	1.055±0.072	(7.06±0.48)	(7.71±0.35)	--
	n-Octane	0.948±0.036	(8.04±0.31)		
	n-Hexane	1.680±0.038	(8.35±0.19)		8.11 ^e
n-Octane	Cyclohexane	1.157±0.027	(7.74±0.18)	(8.03±0.32)	8.42 ^m
	n-Octane	--	--		(8.48±0.10) ^z
					9.70 ^e
	n-Hexane	2.166±0.079	(10.76±0.39)		10.20 ^A
Nonane	Cyclohexane	1.449±0.028	(9.69±0.19)	(10.50±0.26)	10.70 ^w
	n-Octane	1.287±0.017	(10.92±0.14)		(11.30±1.10) ^z
	n-Hexane	2.371±0.073	(11.78±0.36)		11.00 ^e
n-Decane	Cyclohexane	1.668±0.022	(11.16±0.15)	(11.81±0.18)	(12.9±1.00) ^z
	n-Octane	1.401±0.006	(11.88±0.05)		
	n-Hexane	2.371±0.073	(11.78±0.36)		12.30 ^e
n-Undecane	Cyclohexane	1.668±0.022	(11.16±0.15)	(12.78±0.53)	12.50 ^B
	n-Octane	1.588±0.056	(13.50±0.60)		(11.90±2.00) ^p

a: Weighted average $k_{av} = (w_{ref1} k_{ref1} + w_{ref2} k_{ref2} + \dots) / (w_{ref1} + w_{ref2} + \dots)$, where

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

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).

Structure-activity relationships section:

You only compare with one SAR (the Atkinson SAR). This is a missed opportunity, there are several others to choose from (some examples include: Neeb, 2000; Jenkin et al., 2018; McGillen et al., 2024). In the case of Neeb, this is of particular relevance because there is some critical discussion on the use of a ring-strain

correction factor on page 6 (300) of that study, the authors should consider this in their discussion of SAR performance for cyclic compounds. Incidentally, the recent SAR of McGillen et al. (2024) is not currently configured for cyclic compounds, however, I have assessed its performance on the selection of compounds of this paper. This is very easily done by running the Python code of that paper, from which I find that it performs marginally better than Kwok and Atkinson (1995). This, at least for this limited selection of compounds, supports Neeb's statements about ring strain corrections. However, it is most likely the case that more data on cyclic alkanes of differing ring size would be very useful in assessing this further.

Reply:

Thanks for your valuable suggestions! The obtained reaction rate constants were compared with the SAR values of Wilson et al, 2006, Jenkin et al, 2018 and Neeb, 2000 in Sec. 3.2 (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....

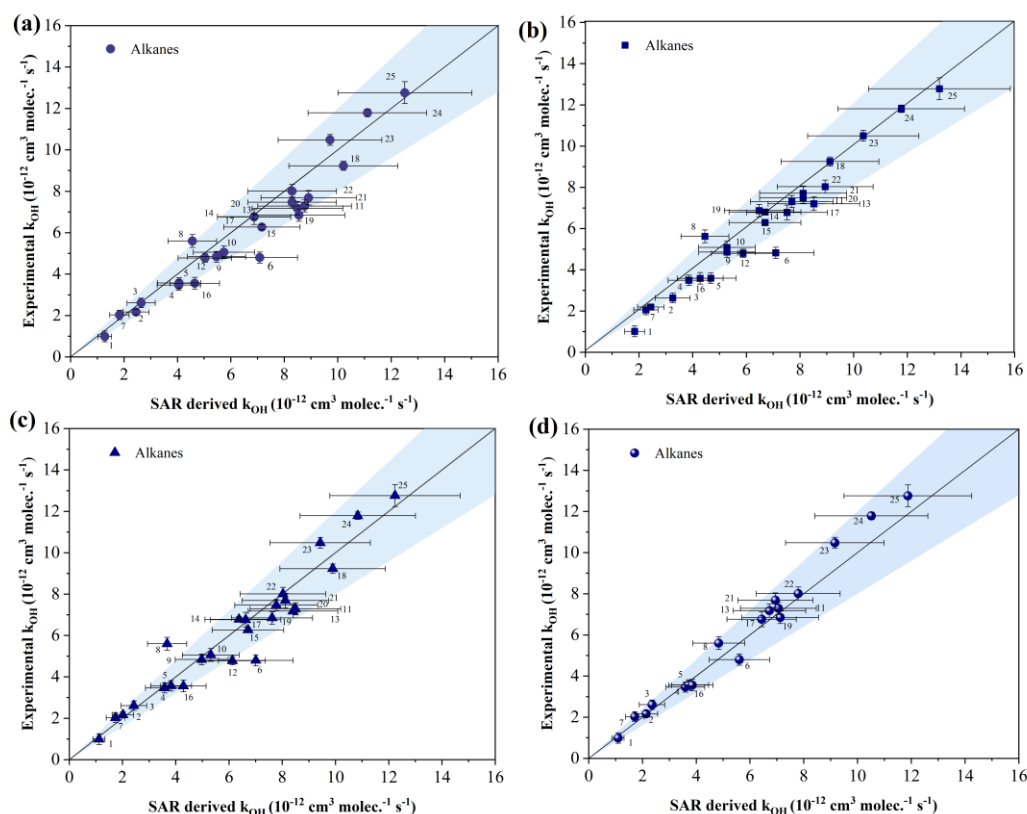


Figure 4. Measured Alkanes + OH rate coefficients plotted against SAR-derived rate coefficients for all compounds (a. Atkinson and Kwok et al., 1995; b. Neeb 2000; c. Jenkin et al. 2018; d. Wilson et al. 2006). The shaded area demonstrates a 20 % uncertainty in the 1:1 black gradient line. The alkanes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

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