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 cm^3 $molecule^{-1}$ s^{-1}) of the three reference compounds selected respectively are expert-evaluated rate constants: $k_{OH+n\text{-}Hexane}$=4.97×10^{-12}, $k_{OH+Cyclohexane}$=6.69×10^{-12}, $k_{OH+n\text{-}Octane}$=8.48×10^{-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 $(1.38\pm0.01)\times10^{-12}$, $(1.25\pm0.03)\times10^{-12}$ and $(1.34\pm0.04)\times10^{-12}$ (the units are cm^3 $molecule^{-1}$ s^{-1}), respectively (within 10%)…..

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…

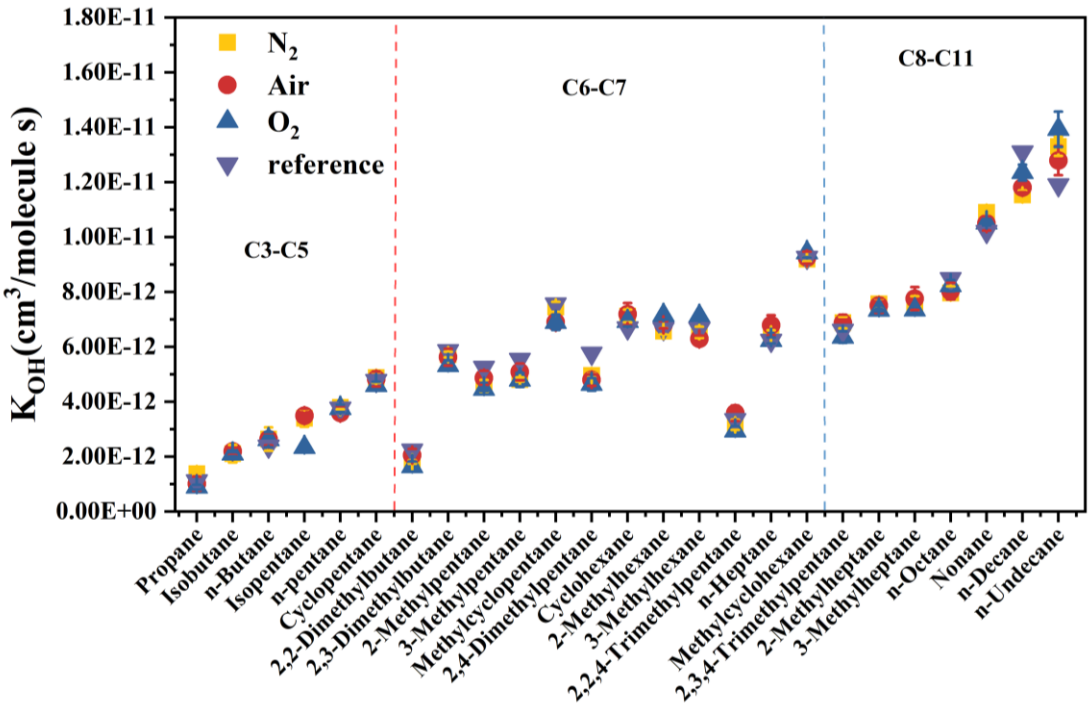

Figure 3. Comparison of rate constants of C3-C11 alkanes in different bath gases (N_2, Air, O_2) with expert-evaluated data at 298±1 K. The error bar was taken as 1σ.

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 literatureat 298±1 K.

Alkanes	Reference	This work			Reference
		$k_{OH}/k_{reference}$ ±1σ	k_{OH} ±1σ (×10^{-12} cm^3 molecule^{-1} s^{-1})	$k_{OH\text{-}av}$[a] ±1σ (×10^{-12} cm^3 molecule^{-1} s^{-1})	k_{OH} (×10^{-12}cm^3 molecule^{-1} s^{-1})
Propane	n-Hexane	0.190±0.033	(9.43±1.66)	(1.01±0.26)	1.11 [bcd] 1.09 [e]
	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] 2.22 [i]
	Cyclohexane	0.315±0.008	(2.08±0.02)		(2.34±0.33) [j]
	n-Octane	0.264±0.005	(2.24±0.04)		
n-Butane	n-Hexane	0.516±0.025	(2.56±0.12)	(2.63±0.23)	(2.36±0.25) [b] (2.72±0.27) [k]
	Cyclohexane	0.398±0.017	(2.66±0.12)		(2.56±0.25) [m]
	n-Octane	0.345±0.042	(2.93±0.36)		(2.46±0.15) [d]
Isopentane	n-Hexane	0.684±0.033	(3.40±0.17)	(3.49±0.25)	3.60 [e] 3.65 [h]
	Cyclohexane	0.512±0.026	(3.43±0.18)		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)	(3.59±0.25)	3.80 [e] 3.98 [n]
	Cyclohexane	0.527±0.021	(3.53±0.14)		4.03 [o]
	n-Octane	0.454±0.029	(3.85±0.24)		(3.97±0.20) [p] (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]
	Cyclohexane	0.711±0.043	(4.76±0.29)		5.02 [q]
	n-Octane	0.600±0.029	(5.09±0.24)		(4.90±0.20) [p] 4.84 [b r]
2,2-Dimethylbutane	n-Hexane	0.409±0.019	(2.03±0.09)	(2.05±0.23)	(2.23±0.15) [p]
	Cyclohexane	0.301±0.030	(2.02±0.20)		2.15 [s]

	n-Octane	0.264±0.031	(2.24±0.26)		2.32 [o]
2,3-Dimethylbutane	n-Hexane Cyclohexane n-Octane	1.095±0.061 0.809±0.039 0.728±0.050	(5.44±0.31) (5.42±0.26) (6.05±0.29)	(5.62±0.31)	5.78 [e] (6.14±0.25) [p] 6.03 [h]
2-Methylpentane	n-Hexane Cyclohexane n-Octane	0.972±0.022 0.722±0.054 0.625±0.045	(4.83±0.11) (4.83±0.36) (5.30±0.38)	(4.86±0.26)	5.2 [e] (5.25±0.25) [p] 5.00 [f] 4.75 [s]
3-Methylpentane	n-Hexane Cyclohexane n-Octane	1.014±0.030 0.777±0.059 0.669±0.082	(5.04±0.15) (5.20±0.40) (5.67±0.70)	(5.08±0.31)	5.20 [e] (5.54±0.25) [p] 4.93 [s]
methylcyclopentane	n-Hexane Cyclohexane n-Octane	1.432±0.053 1.007±0.023 0.849±0.017	(7.12±0.27) (6.73±0.15) (7.00±0.24)	(7.31±0.29)	(7.65±0.10) [u] (8.60±0.30) [p] (8.60±2.20) [t]
2,4-Dimethylpentane	n-Hexane Cyclohexane n-Octane	0.962±0.012 0.721±0.046 0.596±0.026	(4.78±0.06) (4.83±0.31) (5.05±0.22)	(4.80±0.20)	4.80 [e] 5.51 [s] (5.76±0.40) [p]
Cyclohexane	n-Hexane Cyclohexane n-Octane	1.372±0.054 -- 0.872±0.022	(6.82±0.27) -- (7.39±0.19)	(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]
2-Methylhexane	n-Hexane Cyclohexane n-Octane	1.369±0.004 0.993±0.022 0.800±0.031	(6.80±0.02) (6.64±0.15) (6.78±0.26)	(6.80±0.13)	(6.69±0.10) [u]
3-Methylhexane	n-Hexane Cyclohexane n-Octane	1.266±0.003 0.984±0.046 0.807±0.122	(6.29±0.02) (6.58±0.31) (6.73±0.74)	(6.29±0.11)	(6.30±0.10) [u]
2,2,4-Trimethylpentane	n-Hexane Cyclohexane n-Octane	0.702±0.033 0.557±0.032 0.435±0.065	(3.49±0.16) (3.72±0.21) (3.69±0.55)	(3.58±0.28)	3.34 [e] 3.64 [s] (3.34±0.25) [p] (3.71±0.10) [v]
n-Heptane	n-Hexane Cyclohexane n-Octane	1.280±0.066 0.961±0.020 0.828±0.029	(6.36±0.33) (6.43±0.26) (7.03±0.25)	(6.78±0.36)	6.76 [e] 6.68 [y] 6.80 [h] (6.70±0.15) [g]

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] (11.30±1.10) [z]
	Cyclohexane	1.449±0.028	(9.69±0.19)		
	n-Octane	1.287±0.017	(10.92±0.14)		
n-Decane	n-Hexane	2.371±0.073	(11.78±0.36)	(11.81±0.18)	11.00 [e] (12.9±1.00) [z]
	Cyclohexane	1.668±0.022	(11.16±0.15)		
	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] 12.50 [B] (11.90±2.00) [p]
	Cyclohexane	1.668±0.022	(11.16±0.15)		
	n-Octane	1.588±0.056	(13.50±0.60)		

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, 1970b) ; 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, 1970a), 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: $k_{n\text{-}Octane}(T)=(5.07\pm0.97)\times10^{-11}\exp[-(543\pm61)/T]$ cm^3 $molecule^{-1}$ s^{-1}. This 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 and $(4.95\pm0.87)\times10^{-11}\exp[-(531\pm56)/T]$ recommended Arrhenius formula obtained by experts' evaluation of data processing, 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, 1970b) 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: $k_{n\text{-}Heptane}(T)=(5.06\pm0.45)\times10^{-11}\exp[-(602\pm30)/T]$ cm^3 $molecule^{-1}$ s^{-1}. This result agree well with the Arrhenius expression of $(5.20\pm0.54)\times10^{-11}\exp[-(605\pm39)/T]$ $cm^3\cdot molecule^{-1}\cdot s^{-1}$ 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 $k(T)=3.84\times10^{-12}*\exp(148/T)*(T/300)^{1.79}$. Rearrange the fitting data to get the Arrhenius expression in the form of $k(T)=(4.82\pm0.43)\times10^{-11}\exp[-(600\pm31)/T]$ cm^3 $molecule^{-1}$ s^{-1}. Compared with the Arrhenius expression recommended in the literature, the preexponential factor A (5.01±0.42) of this work is agree well with the one (4.82±0.43) of recommended (the unit is 10^{-11} cm^3 $molecule^{-1}$ s^{-1}). However, the activation energy Ea/R of this work is about 60% higher than the recommended data.

C. OH+ Isopentane. As Fig. 5 (c), isopentane was extensively studied over a temperature range (213-407 K). As far as we know, at present, only Wilson et al. has reported this compound in the range of 213-407 K (Wilson et al., 2006). Within the experimental temperature range (273-323 K), our data are consistent with Wilson et al. ((273-323 K), especially in the low temperature range. The Arrhenius expression at 213-407 K obtained by fitting our data and those of Wilson et al. is as follows: $k_{Isopentane}(T)=(1.39\pm0.12)\times10^{-11}\exp[-(424\pm25)/T]$ cm^3 $molecule^{-1}$ s^{-1}. The results are similar to the relative experimental results of Wilson et al. $(1.52\pm0.21)\times10^{-11}\exp[-(432\pm27)/T]$ cm^3 $molecule^{-1}$ s^{-1}.

D. OH+ 2,3-Dimethylbutane. Figure 5 (d) shows the Arrhenius plot for the reaction of 2,3-Dimethylbutane with OH radicals over the temperature range of 273 K to 1366 K. The temperature-dependent values obtained in this study at high temperature (313-323 K) align closely with those reported by Badra and Farooq (Badra and Farooq, 2015), who used the absolute rate technique, as well as the work of Sivaramakrishnan and Michael with a three-parameter fit (Sivaramakrishnan and Michael, 2009). However, the data obtained at 273-293 K in this work are highly consistent with the reviewed data from Atkinson and Arey (Atkinson and Arey, 2003). Linear regression applied to our data and high temperature data in the literature (at 273-1366 K) yields the Arrhenius expression as follows: $k_{2,3\text{-}Dimethylbutane}(T) = (4.81\pm0.56)\times10^{-12}\exp[-(669\pm50)/T]$ cm^3 $molecule^{-1}$ s^{-1}. This result agrees well with the Arrhenius expression of $(4.75\pm0.71)\times10^{-11}\exp[-(664\pm77)/T]$ $cm^3\cdot molecule^{-1}\cdot s^{-1}$ reported by Badra and Farooq (Badra and Farooq, 2015).

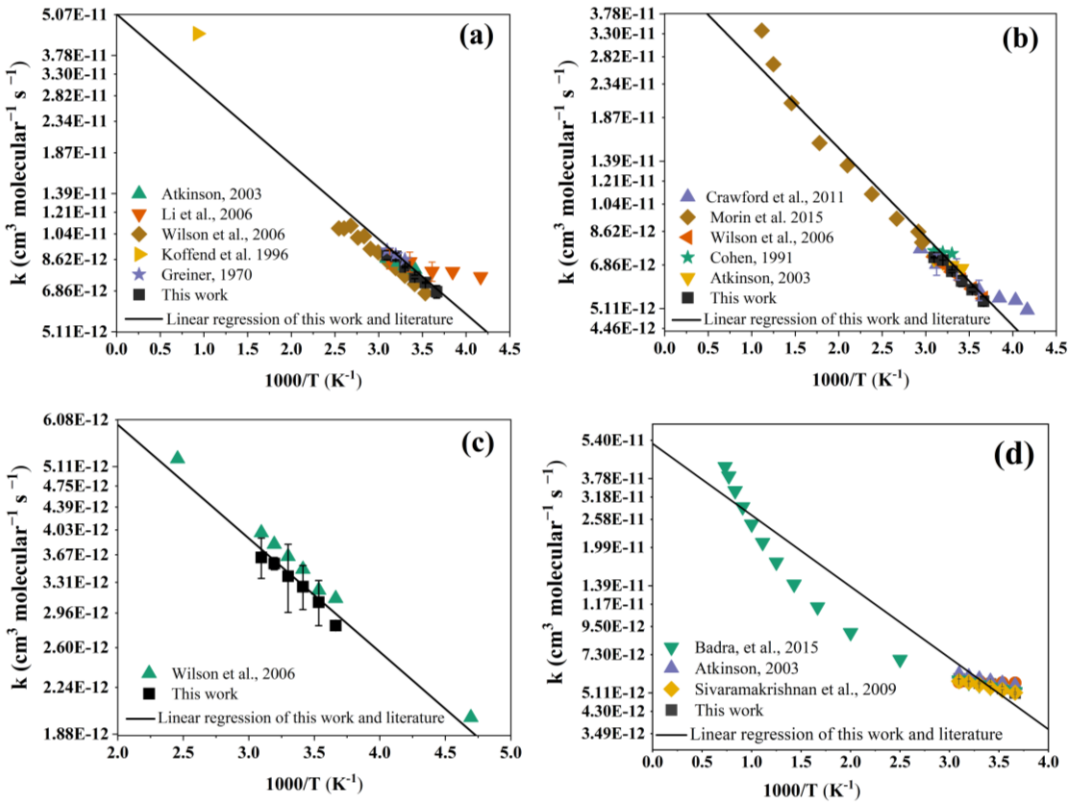

Figure 5. Arrhenius plots for the reaction of n-Octane (a), n-Heptane (b), Isopentane (c) and 2,3-Dimethylbutane (d) with OH radical in wide temperature range

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 $cm^3 \cdot molecule^{-1} \cdot s^{-1}$) 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)
	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)
n-pentane	300-390	2.97	608	AR/EB/LIF	(Donahue et al., 1998)
	224-372	2.45±0.21	516±25	AR/FP/LIF	(Talukdar et al., 1994)
	243-325	--	--	RR/DP/GC	(Harris and Kerr, 1988)
	240-896	5.06±0.45	602±30	RR/DP/GC-FID	this work
	290-1090	1.28±0.21	190	Review	(Atkinson and Arey, 2003)
n-Heptane	241-406	3.38±0.17	497±16	RR/DF/MS	(Wilson et al., 2006)
	240-340	2.25±0.14	293±37	RR/DF/MS	(Crawford et al., 2011)
	248-896	5.2±0.54	605±39	AR/DF/LIF	(Morin et al., 2015)
	298-500	0.0986	600	Theory	(Cohen, 1991)
	240-1080	5.07±0.97	543±61	RR/DP/GC-FID	this work
	240-340	2.27±0.21	296±27	RR/DF/MS	(Li et al., 2006)
	284-384	4.52±0.37	538±27	RR/DF/MS	(Wilson et al., 2006)
n-Octane	290-1080	1.78	235	Review	(Atkinson and Arey, 2003)
	296-497	2.57	332±65	AR/FP/KS	(Greiner, 1970b)
	298-1000	0.0986	600	Theory	(Cohen, 1991)
	273-323	5.29±0.63	520±35	RR/DP/GC-FID	this work
Nonane	240-340	4.35±0.49	411±32	RR/DF/MS	(Li et al., 2006)
	273-323	5.78±0.49	499±25	RR/DP/GC-FID	this work
n-Decane	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)

Isopentane	297-498	0.347	192	AR/FP/GC	(Greiner, 1970b)
	220-407	1.02±0.03	463±10	RR/DF/MS	(Wilson et al., 2006)
	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)
Cyclopentane	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	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	(Sprengnether et al., 2009)
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	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)
	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
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 1σ.

[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.

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, re-forming 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 O_2 in the N_2 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 $(1.38\pm0.01)\times10^{-12}$, $(1.25\pm0.03)\times10^{-12}$ 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 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: $k(T)=(2.43\pm0.52)\times10^{-11}$ exp [–(481.2±60)/T] at 240-340 K was used as the reference compound. Since the research results at room temperature show that different bath gases have little effect on the reaction rate constant, only the temperature dependence of the reaction rate constant under the air system is considered here**...**

….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: $k_{n\text{-}Octane}(T)=(5.07\pm0.97)\times10^{-11}$exp [-(543±61)/T] cm^3 $molecule^{-1}$ s^{-1}. This result agree well with the Arrhenius expression of $(4.52\pm0.37)\times10^{-11}$exp [-(538±27)/T] $cm^3\cdot molecule^{-1}\cdot s^{-1}$ reported by Wilson et al. (Wilson et al., 2006) between 284 and 384 K and $(4.95\pm0.87)\times10^{-11}$exp [-(531±56)/T] recommended Arrhenius formula obtained by experts' evaluation of data processing, but contrast the expressions of $(2.27\pm0.21)\times10^{-11}$exp [-(296±27)/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±65)/T] $cm^3\cdot molecule^{-1}\cdot s^{-1}$ reported by Greiner (Greiner, 1970b) 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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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: $k_{n\text{-}Octane}(T) = (5.07\pm0.97)\times10^{-11}\exp[-(543\pm61)/T]$ cm^3 $molecule^{-1}$ s^{-1}. This 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 and $(4.95\pm0.87)\times10^{-11}\exp[-(531\pm56)/T]$ recommended Arrhenius formula obtained by experts' evaluation of data processing, 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, 1970b) 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…

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} cm^3 $molecule^{-1}$ s^{-1}) was 7.71±0.35. Interestingly, whilst results for n-alkanes agreed well with available structure activity relationship (SAR) calculations, the three cyclo-alkanes and one trimethylpentane were found to be less reactive than predicted by SAR. Conversely, the SAR estimate for 2,3-dimethylbutane were approximately 25% lower than the experimental value, highlighting that the limited understanding of the oxidation chemistry of these compounds. Arrhenius expressions (in units of cm^3 $molecule^{-1}$ s^{-1}) for the reactions of various branched alkanes with OH radical were determined for the first time: 2-methylheptane, $(1.62\pm0.37)\times10^{-11}\exp[-(265\pm70)/T]$, and 3-methylheptane, $(3.54\pm0.45)\times10^{-11}\exp[-(374\pm49)/T]$. The reactivity relation of saturated alkanes with OH radicals and chlorine atoms was obtained: $\log_{10}[k_{(Cl+alkanes)}]$ =

$0.569\times\log_{10}[k_{(OH+alkanes)}]-3.111$ (R^2 =0.86). In addition, the rate coefficients for the 24 previous studied OH + alkanes reactions were consistent with existing literature values, demonstrating the reliability and efficiency of this method for simultaneous investigation of gas-phase reaction kinetics.

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 NO_3 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.

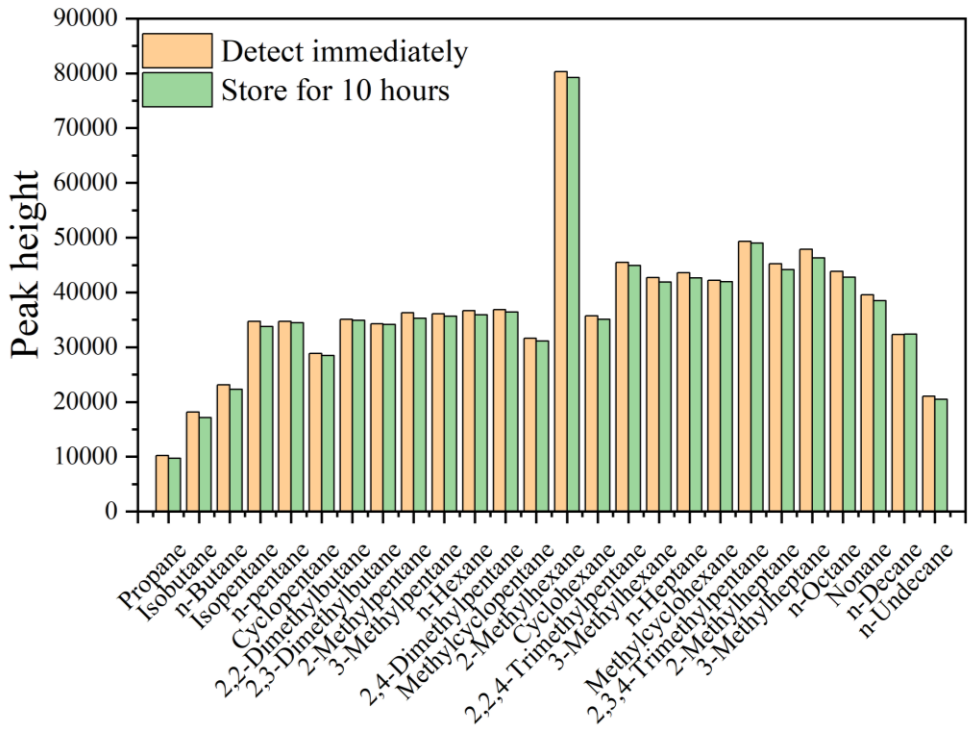

Fig.R1 The VOC loss in PVF bags

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 H_2O_2 respect to VOCs was injected through a three-way valve using a micro syringe. Initial conditions of the different species introduced into the reactor for each experiment are outlined in Table S1 in the Supplementary Material.

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 4.8×10^{-12} cm^3 $molecule^{-1}$ s^{-1}, while the recommended expert-evaluated data of database for Version 2.1.0 of McGillen et al. is 5.76×10^{-12} cm^3 $molecule^{-1}$ 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 cm^3 $molecule^{-1}$ s^{-1}) of the three reference compounds selected respectively are expert-evaluated rate constants: $k_{OH+n\text{-}Hexane}$=4.97×10^{-12}, $k_{OH+Cyclohexane}$=6.69×10^{-12}, $k_{OH+n\text{-}Octane}$=8.48×10^{-12}, which is fitted or manually entered data from multiple sources…

Line 193. Was the H_2O_2 purified?

Reply: Yes! H_2O_2 was obtained 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 comparation 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.

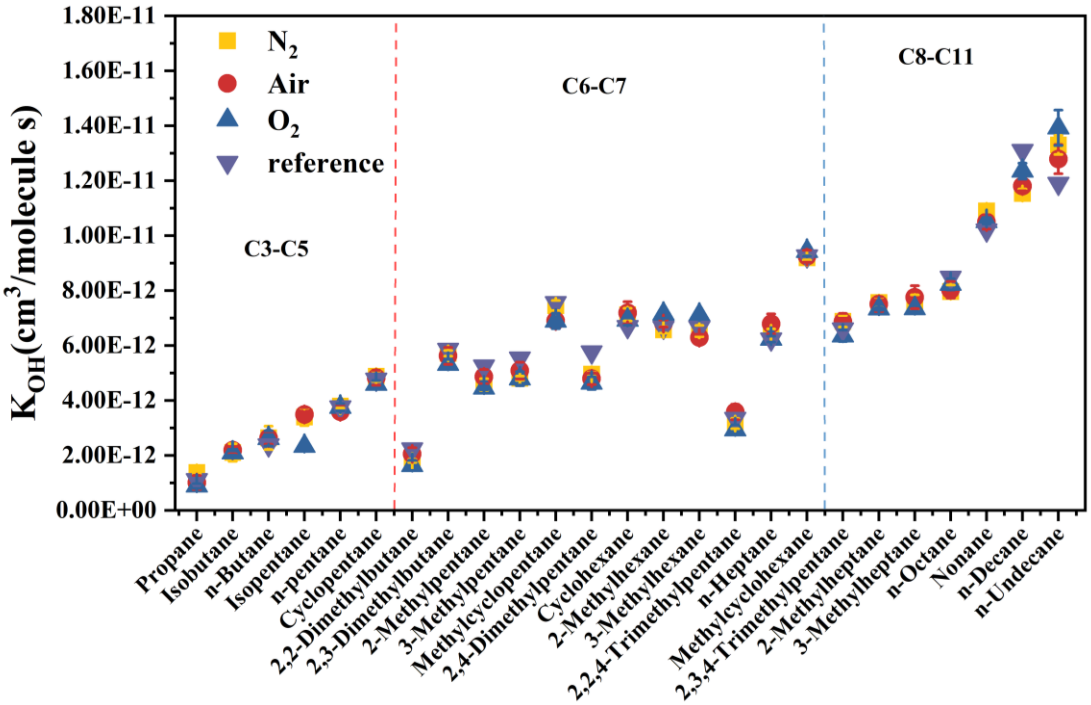

Figure 3. Comparison of rate constants of C3-C11 alkanes in different bath gases (N_2, Air, O_2) with expert-evaluated data at 298±1 K. The error bar was taken as σ.

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

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

	Cyclohexane	1.349±0.012	(9.02±0.08)		(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					9.70 [e]
	n-Hexane	2.166±0.079	(10.76±0.39)		10.20 [A]
	Cyclohexane	1.449±0.028	(9.69±0.19)	(10.50±0.26)	10.70 [w]
	n-Octane	1.287±0.017	(10.92±0.14)		(11.30±1.10) [z]
n-Decane	n-Hexane	2.371±0.073	(11.78±0.36)		11.00 [e]
	Cyclohexane	1.668±0.022	(11.16±0.15)	(11.81±0.18)	(12.9±1.00) [z]
	n-Octane	1.401±0.006	(11.88±0.05)		
n-Undecane	n-Hexane	2.371±0.073	(11.78±0.36)		12.30 [e]
	Cyclohexane	1.668±0.022	(11.16±0.15)	(12.78±0.53)	12.50 [B]
	n-Octane	1.588±0.056	(13.50±0.60)		(11.90±2.00) [p]

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, 1970b) ; 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, 1970a), 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….

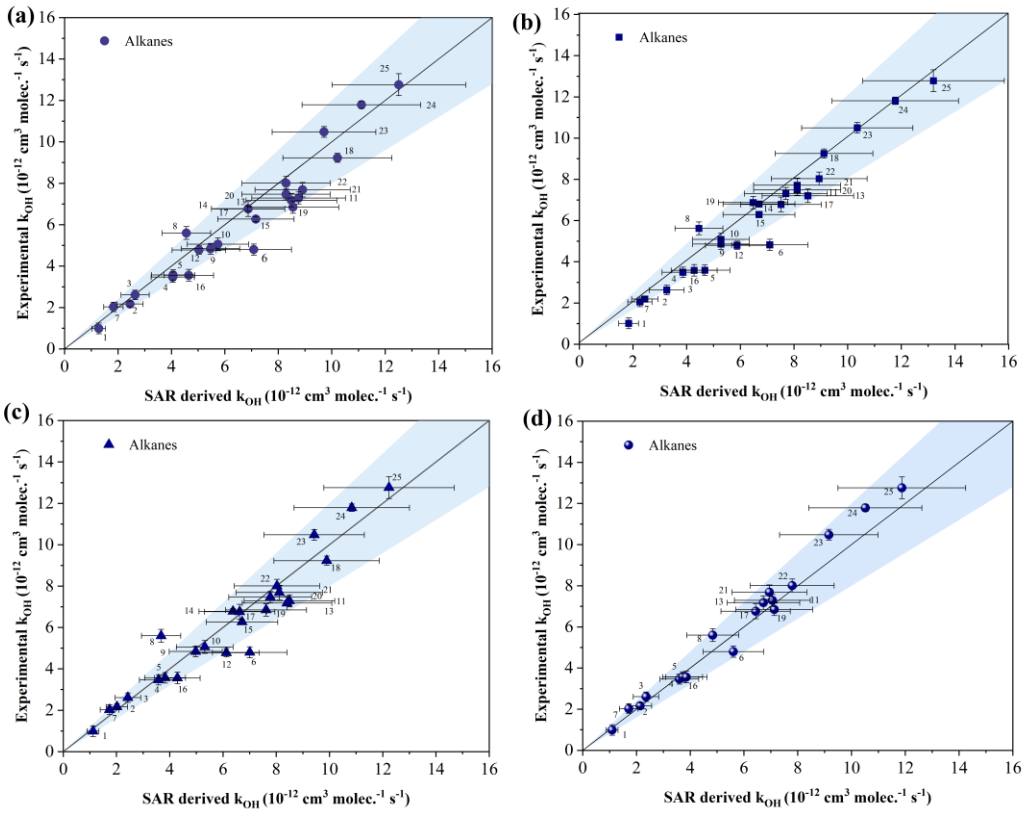

Figure 4. Measured Alkanes + OH rate coefficients plotted against SAR-derived rate coefficients for all compounds (a. Atkinson and Kwok et al., 1995; b. Neeb 2000; c. Jenkin et al. 2018; d. Wilson et al. 2006). The shaded area demonstrates a 20 % uncertainty in the 1:1 black gradient line. The alkanes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

RC2: General Comments

1. Abstract, ln. 15. Please correct "reported were determined" with "reported was determined"

Reply: Sorry for the mistake! The "reported were determined" have been modified to "reported was determined" in the revised manuscript.

…a new room temperature relative rate constant for 3-methylheptane that had not been previously reported was determined…

2. It is highly recommended the authors to correct the rate coefficient capital K throughout the manuscript to avoid confusion with the reaction equilibrium constant. Please use k to refer to the reaction rate coefficient.

Reply: Yes! 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.

…

3. Please avoid using rate constant since k is not a constant, particularly since the authors have also measured the rate coefficient temperature dependence (k(T)). Although rate constant is commonly used it would be better to be more accurate.

Reply: Thanks for your valuable suggestions! We have modified the rate coefficient

symbol k temperature dependence to k(T) in the revised manuscript.

For example: …the derived Arrhenius expressions are as follows: $k_{n\text{-}Octane}(T)=(5.17\pm0.97)\times10^{-11}\exp[-(546\pm60)/T]$ cm^3 molecule^{-1} s^{-1}…

…213-407 K obtained by fitting our data and those of Wilson et al. is as follows: $k_{Isopentane}(T)=(1.39\pm0.12)\times10^{-11}\exp[-(424\pm25)/T]$ cm^3 molecule^{-1} s^{-1}…

…

4. Please replace 'cm^3·molecule^{-1}·s^{-1}' with 'cm^3 molecule^{-1} s^{-1}' throughout the text.

Reply: Thanks for your valuable suggestions! All 'cm^3·molecule^{-1}·s^{-1}' have been replaced with 'cm^3 molecule^{-1} s^{-1}' in the revised manuscript.

5. Please replace OH· and NO_3· with OH and NO_3 radical throughout the text. in the revised manuscript

Reply: Thanks for your valuable suggestions! All instances of OH· and NO_3· have been replaced with OH and NO_3 radical in the revised manuscript.

6. Pg. 2, ln. 47–50. The reason that OH abstraction reactions dominate atmospheric degradation is related to both the faster reactions OH radical initiate along with the relative abundance of the oxidants. So, the at least 5 orders of magnitude slower reactions that NO_3 radical initiate need to be combined with the relative abundance of OH and NO_3 radical during daytime. Please include a sentence to address that or, even better, remove the whole discussion with NO_3 chemistry, since it is out of the scope of this study.

Reply: Thanks for your valuable suggestions! Following your suggestions and those of other reviewers, the discussion involving NO_3 chemistry has been removed from the revised manuscript.

7. Pg 3. Ln. 63–67. The statement in which relative rate and absolute methods are compared (stated twice in the document) is misleading. First, absolute rate measurements are not that rare, and time-resolved measurements have been extensively and very efficiently used in the past by some of the leading groups on

kinetics studies. The recommendation of the present reviewer is to either rephrase or delete this argument (in both places), particularly since the two different techniques have advantages and disadvantages that are not only related to the OH detection difficulties or the accurately measured compound concentrations. Both of the latter should not be an issue nowadays! Secondary photochemistry of different sources is one of the issues that both techniques need to test and combat.

Reply: Thanks for your valuable suggestions! The section comparing relative rate and absolute methods has been revised in the updated 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). From 1980s to 2020s, dozens of papers for the rate coefficients of alkanes with OH radical measured by relative rate mehod have been published…

Major comments:

1. Why the authors didn't use the recommended rate coefficients from the two evaluation panels (IUPAC, NASA/JPL) for the reference reactions and they preferably, where exist? There are some issues with reproducing the quoted data in the tables. Also, in the section where they describe the criteria for reference reaction selections, they have fully omitted one of the most important criteria, which that is the reference reaction rate coefficient needs to be similar to the one under study, to increase measurement sensitivity. Please include. This way both axes range are similar and the concentration variations can be measured with similar precision. Also please include 1σ, not just σ in error analysis and describe if this includes systematic uncertainties (reference reaction rate coefficients are one of the major sources of that in relative rate determinations). In general, error

analysis and references to that are vague. What is the meaning of 2σ levels on SAR? What are the major sources of errors (random and systematic) in their measurements?

Reply: Thanks for the valuable suggestions! The recommended rate coefficients from the panels of IUPAC and NASA/JPL have been added in the revised manuscript. For instance, Table 1 includes database recommendation data, such as, $k_{n\text{-}Heptane}$=6.80×$\mathbf{10^{-12}}$ cm^3 $molecule^{-1}$ s^{-1} (Anderson et al., 2004). 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. Additionally, the format of Table 2 has been adjusted and standardized. For the error analysis mentioned in the manuscript, σ has been modified to 1σ, including systematic uncertainties. As you mentioned, selecting reference compounds with rate coefficients similar to the target reaction rate coefficient is crucial. Further details on the conditions required for relative rate techniques have been included in our 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})	$k_{OH\text{-}av}$[a] ±1σ (×10^{-12} cm^3 $molecule^{-1}$ s^{-1})	k_{OH} (×$10^{-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				(2.19±0.13)	2.12 [h]
	n-Hexane	0.444±0.012	(2.21±0.06)		2.22 [i]
	Cyclohexane	0.315±0.008	(2.08±0.02)		(2.34±0.33) [j]
	n-Octane	0.264±0.005	(2.24±0.04)		

					(2.36±0.25) [b]
	n-Hexane	0.516±0.025	(2.56±0.12)		(2.72±0.27) [k]
n-Butane	Cyclohexane	0.398±0.017	(2.66±0.12)	(2.63±0.23)	(2.56±0.25) [m]
	n-Octane	0.345±0.042	(2.93±0.36)		(2.46±0.15) [d]
					3.60 [e]
	n-Hexane	0.684±0.033	(3.40±0.17)		3.65 [h]
Isopentane	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)		
					3.80 [e]
	n-Hexane	0.709±0.042	(3.52±0.21)		3.98 [n]
n-pentane	Cyclohexane	0.527±0.021	(3.53±0.14)	(3.59±0.25)	4.03 [o]
	n-Octane	0.454±0.029	(3.85±0.24)		(3.97±0.20) [p]
					(4.20±0.15) [g]
					4.97 [e]
	n-Hexane	0.951±0.033	(4.72±0.17)		4.83 [b]
Cyclopentane	Cyclohexane	0.711±0.043	(4.76±0.29)	(4.82±0.27)	5.02 [q]
	n-Octane	0.600±0.029	(5.09±0.24)		(4.90±0.20) [p]
					4.84 [b r]
					(2.23±0.15) [p]
	n-Hexane	0.409±0.019	(2.03±0.09)		2.15 [s]
2,2-Dimethylbutane	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)		
					5.78 [e]
	n-Hexane	1.095±0.061	(5.44±0.31)		(6.14±0.25) [p]
2,3-Dimethylbutane	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)		
					5.2 [e]
	n-Hexane	0.972±0.022	(4.83±0.11)		(5.25±0.25) [p]
2-Methylpentane	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]
					5.20 [e]
	n-Hexane	1.014±0.030	(5.04±0.15)		(5.54±0.25) [p]
3-Methylpentane	Cyclohexane	0.777±0.059	(5.20±0.40)	(5.08±0.31)	4.93 [s]
	n-Octane	0.669±0.082	(5.67±0.70)		
					(7.65±0.10) [u]
	n-Hexane	1.432±0.053	(7.12±0.27)		(8.60±0.30) [p]
methylcyclopentane	Cyclohexane	1.007±0.023	(6.73±0.15)	(7.31±0.29)	(8.60±2.20) [t]
	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]

	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]
					6.97 [e]
					7.14 [q]
	n-Hexane	1.372±0.054	(6.82±0.27)		6.38 [h]
Cyclohexane	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]
	n-Hexane	1.369±0.004	(6.80±0.02)		
2-Methylhexane	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)		
	n-Hexane	1.266±0.003	(6.29±0.02)		
3-Methylhexane	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)		
					3.34 [e]
	n-Hexane	0.702±0.033	(3.49±0.16)		3.64 [s]
2,2,4-Trimethylpentane	Cyclohexane	0.557±0.032	(3.72±0.21)	(3.58±0.28)	(3.34±0.25) [p]
	n-Octane	0.435±0.065	(3.69±0.55)		(3.71±0.10) [v]
					6.76 [e]
	n-Hexane	1.280±0.066	(6.36±0.33)		6.68 [y]
n-Heptane	Cyclohexane	0.961±0.020	(6.43±0.26)	(6.78±0.36)	6.80 [h]
	n-Octane	0.828±0.029	(7.03±0.25)		(6.70±0.15) [g]
					9.60 [e]
					(9.64±0.30) [p]
	n-Hexane	1.906±0.098	(9.48±0.49)		(11.8±1.00) [F]
Methylcyclohexane	Cyclohexane	1.349±0.012	(9.02±0.08)	(9.25±0.22)	(9.50±0.14) [D]
	n-Octane	1.160±0.016	(9.83±0.14)		(9.29±0.10) [u]
	n-Hexane	1.355±0.050	(6.73±0.25)		6.60 [e]
2,3,4-Trimethylpentane	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]
	n-Hexane	1.532±0.062	(7.62±0.31)		
2-Methylheptane	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)		
n-Decane	Cyclohexane	1.668±0.022	(11.16±0.15)	(11.81±0.18)	11.00 [e]
	n-Octane	1.401±0.006	(11.88±0.05)		(12.9±1.00) [z]
	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 $k_{av} = (w_{ref1}k_{ref1}+w_{ref2}k_{ref2}+\ldots)/(w_{ref1}+w_{ref2}+\ldots)$, 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, 1970b) ; 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, 1970a), 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).

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
	235 - 361	1.68	584	RR/DP/GC	(Demore and Bayes, 1999)
	300 - 390	1.34	513	AR/EB/LIF	(Donahue et al., 1998)
n-Butane	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)
	273-323	0.90±0.05	310±17	RR/DP/GC-FID	this work
	233-364	1.94	494	RR/DP/GC	(Demore and Bayes, 1999)
n-pentane	300-390	2.97	608	AR/EB/LIF	(Donahue et al., 1998)
	224-372	2.45±0.21	516±25	AR/FP/LIF	(Talukdar et al., 1994)
	243-325	--	--	RR/DP/GC	(Harris and Kerr, 1988)
	240-896	5.06±0.45	602±30	RR/DP/GC-FID	this work
	290-1090	1.28±0.21	190	Review	(Atkinson and Arey, 2003)
n-Heptane	241-406	3.38±0.17	497±16	RR/DF/MS	(Wilson et al., 2006)
	240-340	2.25±0.14	293±37	RR/DF/MS	(Crawford et al., 2011)
	248-896	5.2±0.54	605±39	AR/DF/LIF	(Morin et al., 2015)
	298-500	0.0986	600	Theory	(Cohen, 1991)
	240-1080	5.07±0.97	543±61	RR/DP/GC-FID	this work
	240-340	2.27±0.21	296±27	RR/DF/MS	(Li et al., 2006)
	284-384	4.52±0.37	538±27	RR/DF/MS	(Wilson et al., 2006)
n-Octane	290-1080	1.78	235	Review	(Atkinson and Arey, 2003)
	296-497	2.57	332±65	AR/FP/KS	(Greiner, 1970b)
	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, 1970b)
Isopentane	220-407	1.02±0.03	463±10	RR/DF/MS	(Wilson et al., 2006)
	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)
Cyclopentane	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
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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	(Sprengnether et al., 2009)
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	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)
	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)
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
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 1σ.

[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.

…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…

2. Although the authors have used O_2, air (N_2/O_2), and N_2, as bath gases test measurements and interpretation analysis is incomplete. In general, it is common that when not enough/excess of O_2 is present in relative rate measurements, it is likely that the radicals are not efficiently scavenged and might initiate secondary chemistry, e.g., reactants – targeted or/and reference – regeneration or even chain chemistry that will result in rate coefficient underestimates or overestimates. Radicals react with O_2 pretty fast, e.g., typically in the order of 10^{-12} cm_3 $molecule^{-1}$ s^{-1} which is in the same range as the understudied reactions. In general, to test this, people run experiments at different O_2 levels to ensure that the rate coefficient is not altered. At pressures close to atmospheric pressure where ~150 Torr of O_2 is present, there is enough of O_2 to scavenge the produced radicals, in most cases, which is not the case when the nonreactive N_2 is used as bath gas – there is always some small amount of O_2 even then. Although in the case of hydrogen metathesis, this does not always result in a problem, depending also on the rate coefficient of the studied reaction and the chemistry involved, it might be an issue for slower reactions that compete with radical oxidation. It would have been nice if the authors had experimentally demonstrated that and if not acknowledged this effect in the interpretation of their results.

Reply: Thanks for your valuable suggestions! As you and other reviewer mentioned, there is always some small amount of O_2 in the N_2 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 $(1.38\pm0.01)\times10^{-12}$, $(1.25\pm0.03)\times10^{-12}$ 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 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: $k(T)=(2.43\pm0.52)\times10^{-11}\exp[-(481.2\pm60)/T]$ 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 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: $k_{n\text{-}Octane}(T)=(5.07\pm0.97)\times10^{-11}\exp[-(543\pm61)/T]$ cm^3 $molecule^{-1}$ s^{-1}. This 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 and $(4.95\pm0.87)\times10^{-11}\exp[-(531\pm56)/T]$ recommended Arrhenius formula obtained by experts' evaluation of data processing, 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, 1970b) 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….

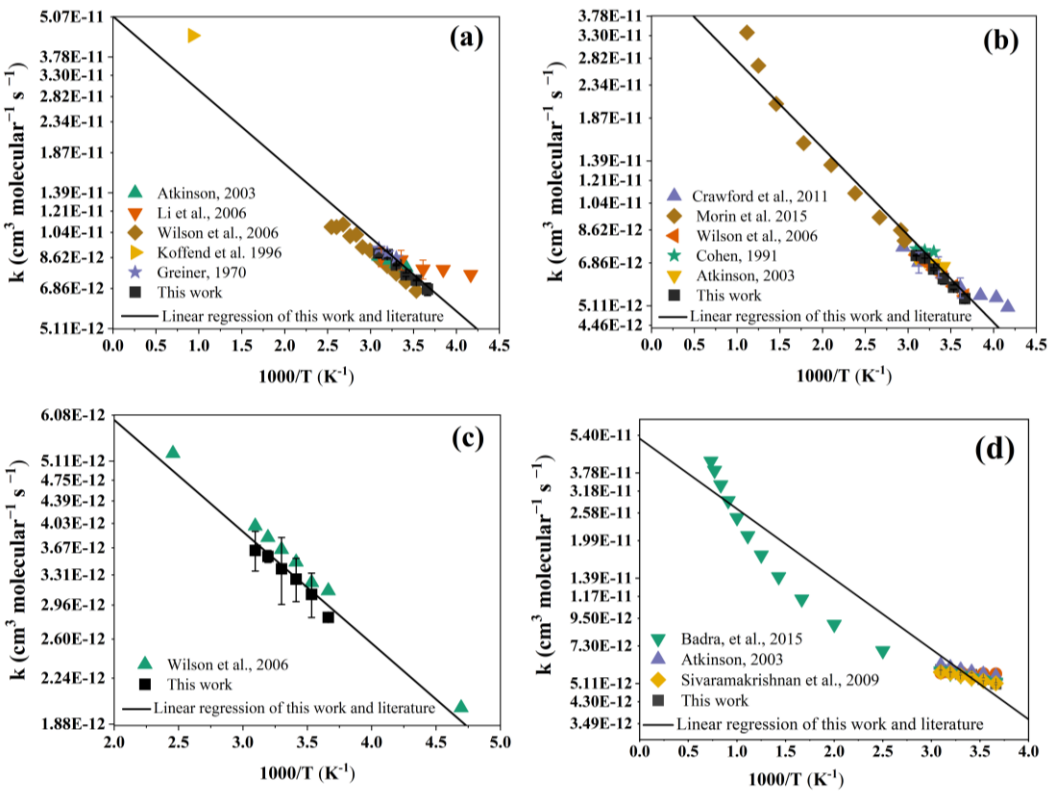

Figure 5. Arrhenius plots for the reaction of n-Octane (a), n-Heptane (b), Isopentane (c) and 2,3-Dimethylbutane (d) with OH radical in wide temperature range along with available literature data. The error bar was taken as 2σ.

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 NO_3 radicals, Cl atoms and ozone (O_3) (Atkinson and Arey, 2003; Shi et al., 2019). These oxidation processes will form a photochemical smog in the presence of NOx and light, causing regional photochemical pollution (Fiore et al., 2005; Ling and Guo, 2014). Additionally, some secondary oxides produced by the oxidation of alkanes can form secondary organic aerosol (SOA) through homogeneous nucleation or condensation onto existing primary particles (Sun et al., 2016). To fully understand the role of alkanes in atmospheric chemistry, accurate chemical reaction rate data is an important criterion for evaluating its reactivity (Shaw et al., 2018)….

…. 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 CH_2 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 O_3 production. The classification discussion of 25 alkanes has been added in the revised manuscript based on your suggestions.

…For each additional CH_2 group from C3-C11, the reaction rate constant increases about 0.95-1.81 (the unit is 10^{-12} cm^3 $molecule^{-1}$ s^{-1}), reflects the fact that the main way is to extract the H atom from the second-order C-H bond. For branching alkanes, for example, 2,2-Dimethylbutane and 2,3-Dimethylbutane, it is obvious that the addition of CH group increases the reaction rate constants with OH radical to a great extent. For cyclic alkanes, such as cyclopentane, methylcyclopentane, cyclohexane and methylcyclohexane, it can also be seen that the reactivity increase with the increase of cycle size. By comparing the reaction rate constant of cyclopentane and cyclohexane (methylcyclopentane and methylcyclohexane), it is found that for cyclic alkanes, each CH_2 group reaction rate increases by about 2.37×10^{-12} cm^3 $molecule^{-1}$ s^{-1}. It can be seen from the reaction rate constant of cyclopentane and methylcyclopentane (cyclohexane and methylcyclohexane) that the reaction rate constant increases about 2.06×10^{-12} cm^3 $molecule^{-1}$ s^{-1} for cycloalkanes with each increase of methyl.

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 O_3. 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 N_2).

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.

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	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	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)
	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
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.

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.

For example: 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 O_2 in the N_2 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 $(1.38\pm0.01)\times10^{-12}$, $(1.25\pm0.03)\times10^{-12}$ 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 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±0.52)×10^{-11} exp [–(481.2±60)/T] at 240-340 K was used as the reference compound. Since the research results at room temperature show that different bath gases have little effect on the reaction rate constant, only the temperature dependence of the reaction rate constant under the air system is considered here**...**

….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: $k_{n\text{-}Octane}$(T)=(5.07±0.97)×10^{-11}exp [-(543±61)/T] cm^3 $molecule^{-1}$ s^{-1}. This result agree well with the Arrhenius expression of (4.52±0.37)×10^{-11}exp [-(538±27)/T] cm^3·$molecule^{-1}$·s^{-1} reported by Wilson et al. (Wilson et al., 2006) between 284 and 384 K and (4.95±0.87)×10^{-11}exp [-(531±56)/T] recommended Arrhenius formula obtained by experts' evaluation of data processing, but contrast the expressions of (2.27±0.21)×10^{-11}exp [-(296±27)/T] cm^3·$molecule^{-1}$·s^{-1} reported by Li et al. between 240 and 340 K (Li et al., 2006) and (2.57)×10^{-11}exp[-(332±65)/T] cm^3·$molecule^{-1}$·s^{-1} reported by Greiner (Greiner, 1970b) 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….

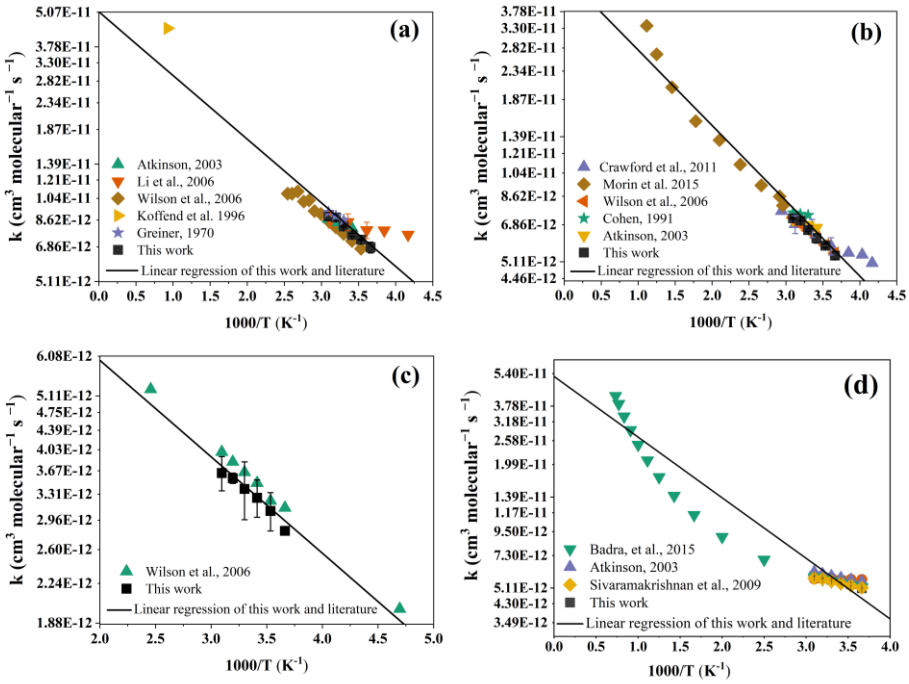

Figure 5. Arrhenius plots for the reaction of n-Octane (a), n-Heptane (b), Isopentane (c) and 2,3-Dimethylbutane (d) with OH radical in wide temperature range along with available literature data. The error bar was taken as 2σ.

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:

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

where τ_{alkane} is the atmospheric lifetime of the alkane due to OH removal, $k_{alkane+OH}$ is the rate constant for the reaction of the alkane with OH radical at the typical tropospheric temperature of 298 K, and [OH] is the atmospheric concentrations of the hydroxyl radicals. The average tropospheric hydroxyl radical concentration has been previously reported in the literature as 1×10^6 molecules cm^{-3} (Li et al., 2018). Using the $k_{alkane+OH}$ (298 K) values determined in the present work, the atmospheric lifetime for 25 alkanes was estimated and listed on the Table 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 O_2 in the atmosphere. The subsequent reaction of alkyl peroxyl radicals enhances the conversion of NO to NO_2 by HO_2 radicals, leading to the production of tropospheric ozone. For short-chain alkanes that stay in the atmosphere for a long time, such as propane, the lifetime is 11d. It should be noted that because the OH concentration is the global average estimated concentration, the applicability of the lifetime may be different in the atmosphere with different OH radical concentrations...

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} cm^3 $molecule^{-1}$ 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±0.56)×10^{-12}exp [-(669±50)/T] cm^3 $molecule^{-1}$ s^{-1}…

Line 104: The figure of the simulation chamber shows a ratio of 200:50 of N_2:O_2 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.

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