

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:

$$k_{n-Octane}(T) = (5.17 \pm 0.97) \times 10^{-11} \exp [-(546 \pm 60)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \dots$$

...213-407 K obtained by fitting our data and those of Wilson et al. is as follows:

$$k_{Isopentane}(T) = (1.39 \pm 0.12) \times 10^{-11} \exp [-(424 \pm 25)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \dots$$

...

4. Please replace ‘cm³·molecule⁻¹·s⁻¹’ with ‘cm³ molecule⁻¹ s⁻¹’ throughout the text.

Reply: Thanks for your valuable suggestions! All ‘cm³·molecule⁻¹·s⁻¹’ have been

replaced with ' $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ' in the revised manuscript.

5. Please replace $\text{OH}\cdot$ and $\text{NO}_3\cdot$ with OH and NO_3 radical throughout the text in the revised manuscript

Reply: Thanks for your valuable suggestions! All instances of $\text{OH}\cdot$ and $\text{NO}_3\cdot$ 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 method 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, $k_{n\text{-Heptane}}=6.80\times 10^{-12}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (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
		$k_{OH}/k_{reference}$ $\pm 1\sigma$	k_{OH} $\pm 1\sigma$ ($\times 10^{-12}$ cm ³ molecule ⁻¹ s ⁻¹)	k_{OH-av}^a $\pm 1\sigma$ ($\times 10^{-12}$ cm ³ molecule ⁻¹ s ⁻¹)
Propane	n-Hexane	0.190 \pm 0.033	(9.43 \pm 1.66)	1.11 ^{bcd} 1.09 ^e
	Cyclohexane	0.153 \pm 0.028	(1.03 \pm 0.18)	1.91 ^f
	n-Octane	0.136 \pm 0.031	(1.16 \pm 0.26)	(1.15 \pm 0.15) ^g
Isobutane	n-Hexane	0.444 \pm 0.012	(2.21 \pm 0.06)	2.12 ^h 2.22 ⁱ
	Cyclohexane	0.315 \pm 0.008	(2.08 \pm 0.02)	(2.19 \pm 0.13)
	n-Octane	0.264 \pm 0.005	(2.24 \pm 0.04)	(2.34 \pm 0.33) ^j
n-Butane	n-Hexane	0.516 \pm 0.025	(2.56 \pm 0.12)	(2.36 \pm 0.25) ^b (2.72 \pm 0.27) ^k
	Cyclohexane	0.398 \pm 0.017	(2.66 \pm 0.12)	(2.56 \pm 0.25) ^m
	n-Octane	0.345 \pm 0.042	(2.93 \pm 0.36)	(2.46 \pm 0.15) ^d
Isopentane	n-Hexane	0.684 \pm 0.033	(3.40 \pm 0.17)	3.60 ^e 3.65 ^h
	Cyclohexane	0.512 \pm 0.026	(3.43 \pm 0.18)	(3.49 \pm 0.25)
	n-Octane	0.442 \pm 0.025	(3.75 \pm 0.22)	3.50 ^f
n-pentane	n-Hexane	0.709 \pm 0.042	(3.52 \pm 0.21)	3.80 ^e 3.98 ⁿ
	Cyclohexane	0.527 \pm 0.021	(3.53 \pm 0.14)	(3.59 \pm 0.25)
	n-Octane	0.454 \pm 0.029	(3.85 \pm 0.24)	4.03 ^o (3.97 \pm 0.20) ^p

					(4.20±0.15) ^g
					4.97 ^e
					4.83 ^b
Cyclopentane	n-Hexane	0.951±0.033	(4.72±0.17)		5.02 ^q
	Cyclohexane	0.711±0.043	(4.76±0.29)	(4.82±0.27)	(4.90±0.20) ^p
	n-Octane	0.600±0.029	(5.09±0.24)		4.84 ^{br}
					(2.23±0.15) ^p
2,2-Dimethylbutane	n-Hexane	0.409±0.019	(2.03±0.09)		2.15 ^s
	Cyclohexane	0.301±0.030	(2.02±0.20)	(2.05±0.23)	2.32 ^o
	n-Octane	0.264±0.031	(2.24±0.26)		
					5.78 ^e
2,3-Dimethylbutane	n-Hexane	1.095±0.061	(5.44±0.31)		(6.14±0.25) ^p
	Cyclohexane	0.809±0.039	(5.42±0.26)	(5.62±0.31)	6.03 ^h
	n-Octane	0.728±0.050	(6.05±0.29)		
					5.2 ^e
2-Methylpentane	n-Hexane	0.972±0.022	(4.83±0.11)		(5.25±0.25) ^p
	Cyclohexane	0.722±0.054	(4.83±0.36)	(4.86±0.26)	5.00 ^f
	n-Octane	0.625±0.045	(5.30±0.38)		4.75 ^s
					5.20 ^e
3-Methylpentane	n-Hexane	1.014±0.030	(5.04±0.15)		(5.54±0.25) ^p
	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
methylcyclopentane	n-Hexane	1.432±0.053	(7.12±0.27)		(8.60±0.30) ^p
	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)		
					4.80 ^e
2,4-Dimethylpentane	n-Hexane	0.962±0.012	(4.78±0.06)		5.51 ^s
	Cyclohexane	0.721±0.046	(4.83±0.31)	(4.80±0.20)	(5.76±0.40) ^p
	n-Octane	0.596±0.026	(5.05±0.22)		6.97 ^e
					7.14 ^q
Cyclohexane	n-Hexane	1.372±0.054	(6.82±0.27)		6.38 ^h
	Cyclohexane	--	--	(7.20±0.33)	6.70 ^b
	n-Octane	0.872±0.022	(7.39±0.19)		(7.19±0.10) ^u
					(6.85±0.20) ^p
					1.369±0.004
2-Methylhexane	n-Hexane	1.369±0.004	(6.80±0.02)		(6.69±0.10) ^u
	Cyclohexane	0.993±0.022	(6.64±0.15)	(6.80±0.13)	
	n-Octane	0.800±0.031	(6.78±0.26)		
					1.266±0.003
3-Methylhexane	n-Hexane	1.266±0.003	(6.29±0.02)		(6.30±0.10) ^u
	Cyclohexane	0.984±0.046	(6.58±0.31)	(6.29±0.11)	

	n-Octane	0.807±0.122	(6.73±0.74)		
					3.34 ^e
2,2,4- Trimethylpentane	n-Hexane	0.702±0.033	(3.49±0.16)		3.64 ^s
	Cyclohexane	0.557±0.032	(3.72±0.21)	(3.58±0.28)	(3.34±0.25) ^p
	n-Octane	0.435±0.065	(3.69±0.55)		(3.71±0.10) ^v
					6.76 ^e
n-Heptane	n-Hexane	1.280±0.066	(6.36±0.33)		6.68 ^y
	Cyclohexane	0.961±0.020	(6.43±0.26)	(6.78±0.36)	6.80 ^h
	n-Octane	0.828±0.029	(7.03±0.25)		(6.70±0.15) ^g
					9.60 ^e
Methylcyclohexane	n-Hexane	1.906±0.098	(9.48±0.49)		(9.64±0.30) ^p
	Cyclohexane	1.349±0.012	(9.02±0.08)	(9.25±0.22)	(11.8±1.00) ^f
	n-Octane	1.160±0.016	(9.83±0.14)		(9.50±0.14) ^d (9.29±0.10) ^u
					6.60 ^e
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)		
					8.11 ^e
n-Octane	n-Hexane	1.680±0.038	(8.35±0.19)		8.42 ^m
	Cyclohexane	1.157±0.027	(7.74±0.18)	(8.03±0.32)	(8.48±0.10) ^z
	n-Octane	--	--		
					9.70 ^e
Nonane	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
					11.00 ^e
n-Decane	n-Hexane	2.371±0.073	(11.78±0.36)		11.00 ^e
	Cyclohexane	1.668±0.022	(11.16±0.15)	(11.81±0.18)	(12.9±1.00) ^z
	n-Octane	1.401±0.006	(11.88±0.05)		
n-Undecane	n-Hexane	2.371±0.073	(11.78±0.36)		12.30 ^e
	Cyclohexane	1.668±0.022	(11.16±0.15)	(12.78±0.53)	12.50 ^B
	n-Octane	1.588±0.056	(13.50±0.60)		(11.90±2.00) ^p

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

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

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

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)

n-pentane	273-323	0.90±0.05	310±17	RR/DP/GC-FID	this work
	233-364	1.94	494	RR/DP/GC	(Demore and Bayes, 1999)
	300-390	2.97	608	AR/EB/LIF	(Donahue et al., 1998)
	224-372	2.45±0.21	516±25	AR/FP/LIF	(Talukdar et al., 1994)
	243-325	--	--	RR/DP/GC	(Harris and Kerr, 1988)
n-Heptane	240-896	5.06±0.45	602±30	RR/DP/GC-FID	this work
	290-1090	1.28±0.21	190	Review	(Atkinson and Arey, 2003)
	241-406	3.38±0.17	497±16	RR/DF/MS	(Wilson et al., 2006)
	240-340	2.25±0.14	293±37	RR/DF/MS	(Crawford et al., 2011)
	248-896	5.2±0.54	605±39	AR/DF/LIF	(Morin et al., 2015)
	298-500	0.0986	600	Theory	(Cohen, 1991)
	240-1080	5.07±0.97	543±61	RR/DP/GC-FID	this work
n-Octane	240-340	2.27±0.21	296±27	RR/DF/MS	(Li et al., 2006)
	284-384	4.52±0.37	538±27	RR/DF/MS	(Wilson et al., 2006)
	290-1080	1.78	235	Review	(Atkinson and Arey, 2003)
	296-497	2.57	332±65	AR/FP/KS	(Greiner, 1970a)
	298-1000	0.0986	600	Theory	(Cohen, 1991)
Nonane	273-323	5.29±0.63	520±35	RR/DP/GC-FID	this work
	240-340	4.35±0.49	411±32	RR/DF/MS	(Li et al., 2006)
n-Decane	273-323	5.78±0.49	499±25	RR/DP/GC-FID	this work
	240-340	2.26±0.28	160±36	RR/DF/MS	(Li et al., 2006)
Isobutane	273-323	2.29±0.74	739±94	RR/DP/GC-FID	this work
	300-390	0.626	321	AR/EB/LIF	(Donahue et al., 1998)
	213-372	0.572	293	AR/FP/LIF	(Talukdar et al., 1994)
	297-498	0.347	192	AR/FP/GC	(Greiner, 1970a)
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)
Cyclopentane	273-323	3.67±0.63	619±51	RR/DP/GC-FID	this work
	288-407	2.71	526	RR/DP/GC	(Wilson et al., 2006)
	240-340	2.43±0.50	481±58	RR/DF/MS	(Singh et al., 2013)
	273 - 423	2.57	498	RR/DP/GC	(Demore and Bayes, 1999)

	300-390	1.88	352	AR/EB/LIF	(Donahue et al., 1998)
	295-491	2.29±0.09	457±0.14	AR/FP/LIF	(Droege and Tully, 1987)
Cyclohexane	273-323	3.62±0.59	522±48	RR/DP/GC-FID	this work
	240-340	3.96±0.60	554±42	RR/DF/MS	(Singh et al., 2013)
	288-408	3.40	513	RR/DP/GC	(Wilson et al., 2006)
Methylcyclopentane	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)
2-Methylhexane	297-1362	6.43±0.87	834±74	AR/DF/LIF	(Badra and Farooq, 2015)
	273-385	1.82±0.09	321±16	RR/DP/GC-FID	this work
3-Methylhexane	230 - 385	1.21±0.07	171±16	AR/DF/LIF	(Sprengnether et al., 2009)
	273-323	2.53±1.45	575±161	RR/DP/GC-FID	this work

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

^{a, b}The error bar was taken as 1σ .

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

...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 O₂, air (N₂/O₂), and N₂, as bath gases test measurements and interpretation analysis is incomplete. In general, it is common

that when not enough/excess of O₂ 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 O₂ pretty fast, e.g., typically in the order of 10⁻¹² cm³ molecule⁻¹ s⁻¹ which is in the same range as the understudied reactions. In general, to test this, people run experiments at different O₂ levels to ensure that the rate coefficient is not altered. At pressures close to atmospheric pressure where ~150 Torr of O₂ is present, there is enough of O₂ to scavenge the produced radicals, in most cases, which is not the case when the nonreactive N₂ is used as bath gas – there is always some small amount of O₂ 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 O₂ in the N₂ bath gas, the impact of bath gas has been reduced in our revised manuscript. For example, the study on relative rate experiments and temperature dependence in different bath gases in Section 3.1 and 3.3 have been removed, with the discussion now centered on the temperature dependence relationship in the air system.

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

The rate constants for the reactions involving OH radical with C3-C11 alkanes in the mixed system were determined at 298±1 K. The concentration curves of target alkanes and the reference compound (n-Hexane) were plotted in Fig. 2. As shown in Fig. 2, the decay of both target and reference compounds correlated well with eq. (7), and high correlation coefficients (R²) were observed for most alkanes, exceeding 0.99. Table 1 and Table S4 listed the obtained *k*_{OH} for C3-C11 alkanes under three bath gases using the related reference compounds. The error bars (1σ) in Table 1 accounted for reference

rate constant uncertainty, and experimental parameter uncertainties (pressure, temperature, flow rate, reactant concentration). The results indicated strong agreement (within <15%) between rate constants for 25 C3-C11 straight-chain, branched-chain, and cycloalkanes, using different reference compounds. For example, the k_{OH} obtained for propane with n-hexane, cyclohexane and n-octane as the reference compound were $(1.38\pm 0.01)\times 10^{-12}$, $(1.25\pm 0.03)\times 10^{-12}$ and $(1.34\pm 0.04)\times 10^{-12}$ (the units are $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$), respectively (within 10%). This suggests that reference compound variation minimally affects results, indicating reliable experimental methods and data. Notably, the rate constant for 3-Methylheptane's reaction with OH radicals at room temperature was determined for the first time. As shown in Fig. 3, for the different bath gases, the obtained k_{OH} for C3-C11 alkanes showed high agreement. Meanwhile, it can also be observed from the figure that most of the rate coefficients obtained are very similar to the expert-evaluated values of the database by the McGillen et al. However, 2,4-Dimethylpentane is an exception, the k_{OH} value obtained in this study is about 20% lower than the recommended value...

....3.3 Temperature dependence (273-323 K)

In order to study the relationship between temperature and reaction rate constant, this study carried out experiments in the tropospheric temperature range (273-323 K), and combined with the literature data (the expert-recommended data from database for Version 2.1.0 of McGillen et al.) to study the kinetic temperature dependence of several alkanes in a wide temperature range. And n-hexane (Arrhenius expression: $k(T)=(2.43\pm 0.52)\times 10^{-11} \exp [-(481.2\pm 60)/T]$ at 240-340 K was used as the reference compound. Since the research results at room temperature show that different bath gases have little effect on the reaction rate constant, only the temperature dependence of the reaction rate constant under the air system is considered here...

....A. OH+ n-Octane. Figure 5 (a) exhibits the Arrhenius plot for the reaction between n-Octane and OH radicals, covering a temperature range of 240 to 1080 K. Within the experimental temperature range (273-323 K), our data align well with previous studies. Fit our data to expert-evaluated data (manually entered data from multiple sources), the derived Arrhenius expressions are as follows:

$k_{n\text{-Octane}}(T) = (5.07 \pm 0.97) \times 10^{-11} \exp [-(543 \pm 61)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This result agrees well with the Arrhenius expression of $(4.52 \pm 0.37) \times 10^{-11} \exp [-(538 \pm 27)/T] \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ reported by Wilson et al. (Wilson et al., 2006) between 284 and 384 K and $(4.95 \pm 0.87) \times 10^{-11} \exp [-(531 \pm 56)/T]$ recommended Arrhenius formula obtained by experts' evaluation of data processing, but contrast the expressions of $(2.27 \pm 0.21) \times 10^{-11} \exp [-(296 \pm 27)/T] \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ reported by Li et al. between 240 and 340 K (Li et al., 2006) and $(2.57) \times 10^{-11} \exp [-(332 \pm 65)/T] \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ reported by Greiner (Greiner, 1970a) between 296 and 497 K. By comparison, our data are highly consistent with the data recommended by experts. The obtained Arrhenius expression more accurately represents the relationship between the reaction rate constant of octane and OH radicals and temperature in a wide temperature range, which has certain reference significance....

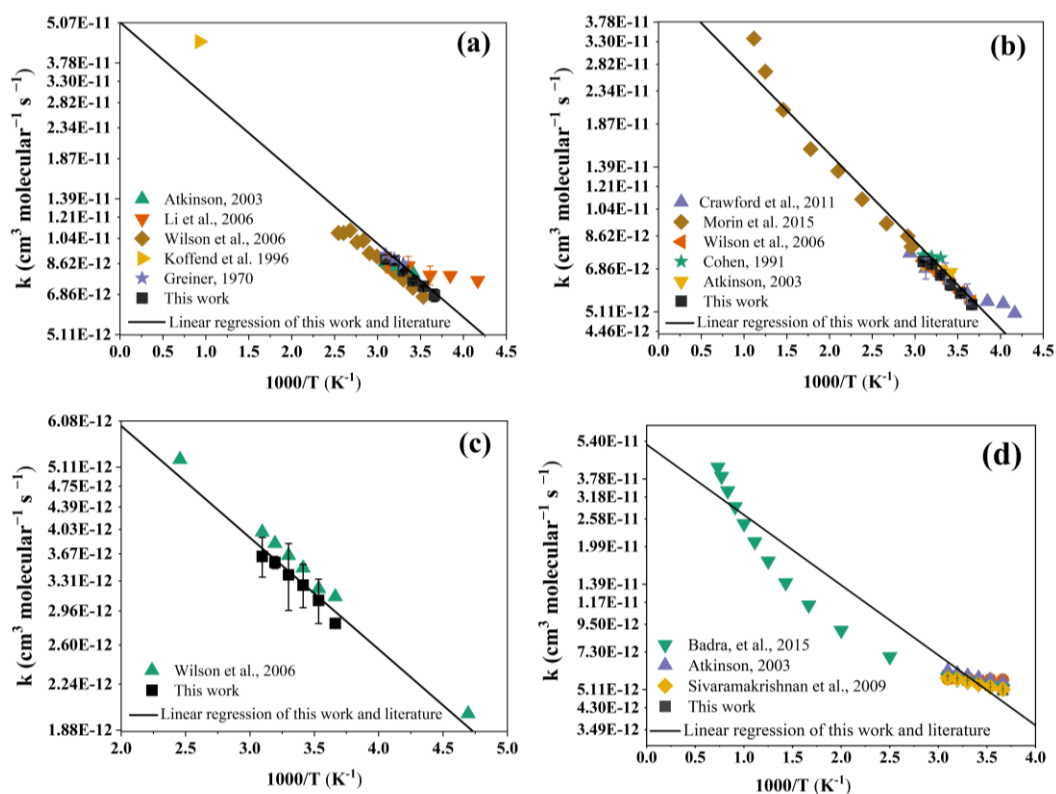


Figure 5. Arrhenius plots for the reaction of n-Octane (a), n-Heptane (b), Isopentane (c) and 2,3-Dimethylbutane (d) with OH radical in wide temperature range along with available literature data. The error bar was taken as 2σ .

References:

- Anderson, R. S., Huang, L., Iannone, R., Thompson, A. E., and Rudolph, J.: Carbon kinetic isotope effects in the gas phase reactions of light alkanes and ethene with the OH radical at 296 ± 4 K, *J. Phys. Chem. A*, 108, 11537-11544, 10.1021/jp0472008, 2004.
- Atkinson, R.: Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds under atmospheric conditions, *Chem. Rev.*, 86, 69-201, 10.1021/cr00071a004, 1986.
- Atkinson, R.: Kinetics of the gas-phase reactions of OH radicals with alkanes and cycloalkanes, *Atmos. Chem. Phys.*, 3, 2233-2307, 10.5194/acp-3-2233-2003, 2003.
- Atkinson, R. and Arey, J.: Atmospheric degradation of volatile organic compounds, *Chem. Rev.*, 103, 4605-4638, 10.1021/cr0206420, 2003.
- Atkinson, R., Aschmann, S. M., Carter, W. P. L., Winer, A. M., and Pitts Jr., J. N.: Kinetics of the reactions of OH radicals with n-alkanes at 299 ± 2 K, *Int. J. Chem. Kinet.*, 14, 781-788, <https://doi.org/10.1002/kin.550140706>, 1982.
- Badra, J. and Farooq, A.: Site-specific reaction rate constant measurements for various secondary and tertiary H-abstraction by OH radicals, *Combust. Flame*, 162, 2034-2044, <https://doi.org/10.1016/j.combustflame.2015.01.001>, 2015.
- Ballesteros, B., Ceacero-Vega, A. A., Jimenez, E., and Albaladejo, J.: Atmospheric reactions of methylcyclohexanes with Cl atoms and OH radicals: determination of rate coefficients and degradation products, *Environ Sci Pollut Res Int*, 22, 4806-4819, <https://doi.org/10.1007/s11356-014-2901-0>, 2015.
- Bejan, I. G., Winiberg, F. A. F., Mortimer, N., Medeiros, D. J., Brumby, C. A., Orr, S. C., Kelly, J., and Seakins, P. W.: Gas-phase rate coefficients for a series of alkyl cyclohexanes with OH radicals and Cl atoms, *International Journal of Chemical Kinetics*, 50, 544-555, 10.1002/kin.21179, 2018.
- Bryukov, M. G., Knyazev, V. D., Lomnicki, S. M., McFerrin, C. A., and Dellinger, B.: Temperature-dependent kinetics of the gas-phase reactions of OH with Cl₂, CH₄, and C₃H₈, *J. Phys. Chem. A*, 108, 10464-10472, 10.1021/jp047340h, 2004.
- Calvert, J. G., Orlando, J. J., Stockwell, W. R., and Wallington, T. J.: *The mechanisms of reactions influencing atmospheric ozone*, Oxford University Press, Incorporated, New York, UNITED STATES 2015.
- Cohen, N.: Are reaction rate coefficients additive? Revised transition state theory calculations for OH + alkane reactions, *International Journal of Chemical Kinetics*, 23, 397-417, <https://doi.org/10.1002/kin.550230506>, 1991.
- Cox, R. A., Derwent, R. G., and Williams, M. R.: Atmospheric photooxidation reactions. rates, reactivity, and mechanism for reaction of organic compounds with hydroxyl radicals, *Environ. Sci. Technol.*, 14, 57-61, 10.1021/es60161a007, 1980.
- Crawford, M. A., Dang, B., Hoang, J., and Li, Z.: Kinetic study of OH radical reaction with n-heptane and n-hexane at 240–340K using the relative rate/discharge flow/mass spectrometry (RR/DF/MS) technique, *International Journal of Chemical Kinetics*, 43, 489-497, <https://doi.org/10.1002/kin.20574>, 2011.
- DeMore, W. and Bayes, K.: Rate constants for the reactions of hydroxyl radical with several alkanes, cycloalkanes, and dimethyl ether, *The Journal of Physical Chemistry A*, 103, 2649-2654, 1999.
- Donahue, N. M., Anderson, J. G., and Demerjian, K. L.: New rate constants for ten OH alkane reactions from 300 to 400 K: an assessment of accuracy, *The Journal of Physical Chemistry A*, 102, 3121-3126, 1998.

- Droege, A. T. and Tully, F. P.: Hydrogen-atom abstraction from alkanes by hydroxyl radical. 6. cyclopentane and cyclohexane, *Journal of Physical Chemistry*, 91, 1222-1225, 1987.
- Edney, E., Kleindienst, T., and Corse, E.: Room temperature rate constants for the reaction of OH with selected chlorinated and oxygenated hydrocarbons, *International journal of chemical kinetics*, 18, 1355-1371, 10.1002/kin.550181207, 1986.
- Ferrari, C., Roche, A., Jacob, V., Foster, P., and Baussand, P.: Kinetics of the reaction of OH radicals with a series of esters under simulated conditions at 295 K, *International Journal of Chemical Kinetics*, 28, 609-614, 10.1002/(sici)1097-4601(1996)28:8<609::Aid-kin6>3.0.Co;2-z, 1996.
- Gordon, S. and Mulac, W.: Reaction of the OH ($X \cdot 71'$) radical produced by the pulse radiolysis of water vapor *Int. J. Chem. Kinet.*, (Syrnp. 1), 289, 299, 1975.
- Greiner, N. R.: Hydroxyl Radical Kinetics by Kinetic Spectroscopy. VI. Reactions with Alkanes in the Range 300–500°K, *J. Chem. Phys.*, 53, 1070-&, 10.1063/1.1674099, 1970a.
- Greiner, N. R.: Comparison of the Kinetics of Alkane H-Atom Abstraction by Methyl and Hydroxyl Radicals, *The Journal of Chemical Physics*, 53, 1285-1287, 10.1063/1.1674134, 1970b.
- Harris, S. J. and Kerr, J. A.: Relative Rate Measurements of Some Reactions of Hydroxyl Radicals with Alkanes Studied under Atmospheric Conditions, *International Journal of Chemical Kinetics*, 20, 939-955, 10.1002/kin.550201203, 1988.
- Li, Z. J., Singh, S., Woodward, W., and Dang, L.: Kinetics study of OH radical reactions with n-octane, n-nonane, and n-decane at 240-340 K using the relative rate/discharge flow/mass spectrometry technique, *J. Phys. Chem. A*, 110, 12150-12157, 10.1021/jp0638134, 2006.
- Mellouki, A., Téton, S., Laverdet, G., Quilgars, A., and Le Bras, G.: Kinetic studies of OH reactions with H₂O₂, C₃H₈ and CH₄ using the pulsed laser photolysis-laser induced fluorescence method, *Journal de chimie physique*, 91, 473-487, 1994.
- Morin, J., Romanias, M. N., and Bedjanian, Y.: Experimental Study of the Reactions of OH Radicals with Propane, n-Pentane, and n-Heptane over a wide temperature range, *International Journal of Chemical Kinetics*, 47, 629-637, <https://doi.org/10.1002/kin.20936>, 2015.
- Perry, R. A., Atkinson, R., and Pitts, J. N.: Rate constants for the reaction of OH radicals with nbutane over the temperature range 297–420°K, *J. Chem. Phys.*, 64, 5314-5316, 10.1063/1.432167, 1976.
- Shaw, J. T., Rickard, A. R., Newland, M. J., and Dillon, T. J.: Rate coefficients for reactions of OH with aromatic and aliphatic volatile organic compounds determined by the multivariate relative rate technique, *Atmospheric Chemistry and Physics*, 20, 9725-9736, 10.5194/acp-20-9725-2020, 2020.
- Singh, S., de Leon, M. F., and Li, Z. J.: Kinetics Study of the Reaction of OH Radicals with C₅-C₈ Cycloalkanes at 240-340 K using the Relative Rate/Discharge Flow/Mass Spectrometry Technique, *J. Phys. Chem. A*, 117, 10863-10872, 10.1021/jp406923d, 2013.
- Sivaramakrishnan, R. and Michael, J. V.: Rate constants for OH with selected large alkanes: shock-tube measurements and an improved group scheme, *J. Phys. Chem. A*, 113, 5047-5060, 10.1021/jp810987u, 2009.
- Sprengnether, M. M., Demerjian, K. L., Dransfield, T. J., Clarke, J. S., Anderson, J. G., and Donahue, N. M.: Rate Constants of Nine C₆-C₉ Alkanes with OH from 230 to 379 K: Chemical Tracers for OH, *J. Phys. Chem. A*, 113, 5030-5038, 10.1021/jp810412m, 2009.
- Talukdar, R. K., Mellouki, A., Gierczak, T., Barone, S., Chiang, S. Y., and Ravishankara, A. R.: Kinetics of the reactions of OH with alkanes, *International Journal of Chemical Kinetics*, 26, 973-990, 10.1002/kin.550261003, 1994.

Tully, F. P., Goldsmith, J. E. M., and Droege, A. T.: Hydrogen-Atom Abstraction from Alkanes by OH.
4. Isobutane, *Journal of Physical Chemistry*, 90, 5932-5937, 10.1021/j100280a095, 1986.

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