**RC1:**

**Line 37-38 Please revise the sentence since the alkanes are extremely less reactive with $NO_3$ and ano reacting with ozone.**

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

…In the troposphere, the alkanes are extremely less reactive with $NO_3$ and ano reacting with ozone, they are degraded and removed from the atmosphere via gas-phase oxidation reactions with OH radicals and chlorine atoms…..

**Line 41: Replace "some secondary oxides" with degradation products.**

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

…Additionally, degradation products produced by the oxidation of alkanes can form…

**Line 47: There are not only these two methods used for absolute measurements.**

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

…(such as flash photolysis and emission flow et al.)…

**Line 74: "Finlaysonpitts et al"**

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

Finlaysonpitts, B. J. and Pitts, J. N., Jr.: Tropospheric air pollution: ozone, airborne toxics, polycyclic aromatic hydrocarbons, and particles, Science (New York, N.Y.), 276, https://doi.org/1045-1052, 10.1126/science.276.5315.1045, 1997.

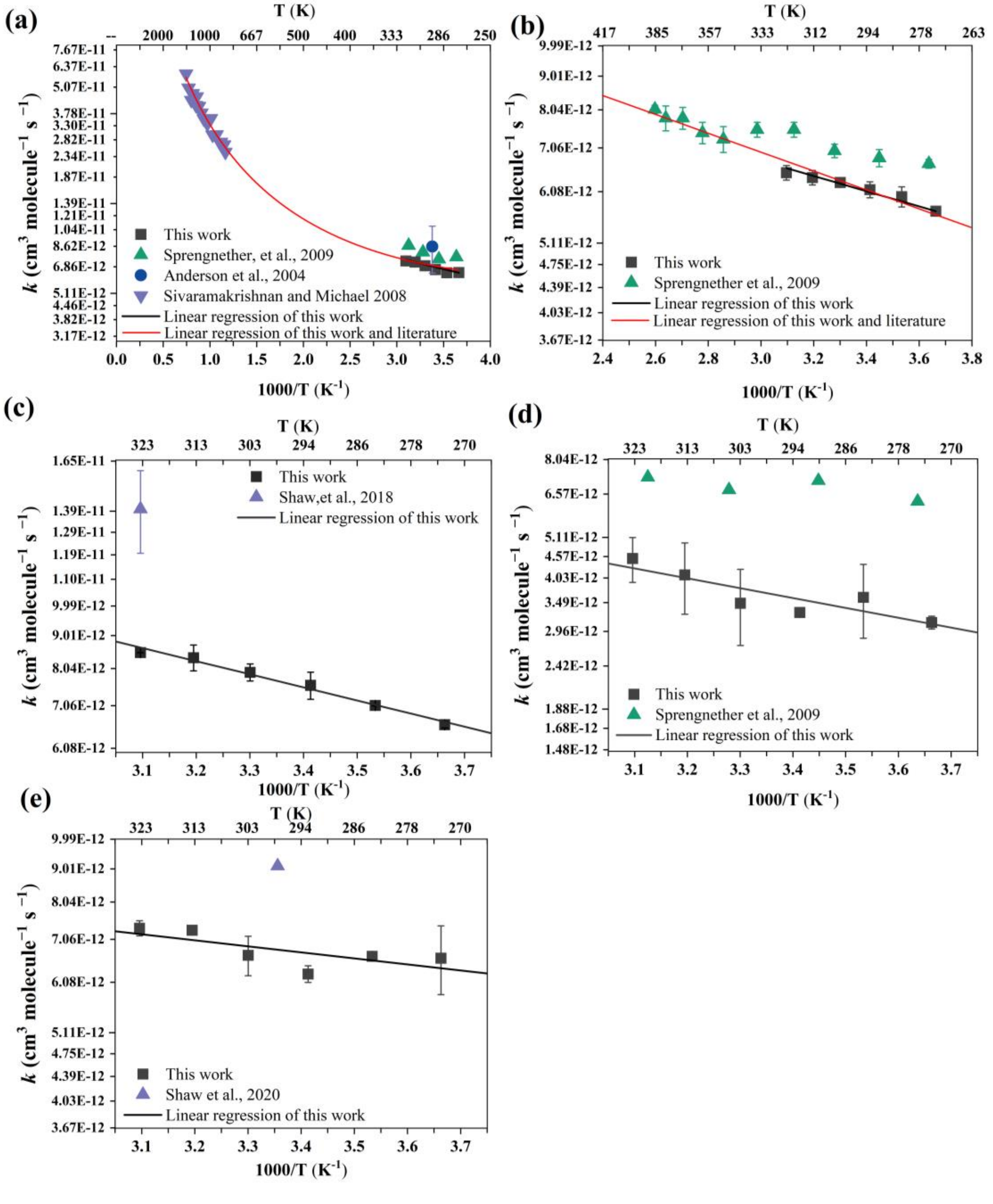
**Line 225: "RCH2R", there is better to add R1CH2R2**

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

…the reactivity of linear alkanes ($R_1CH_2R_2$) with OH radicals increasing…

**Line 475: Please revise the linear regression fit for figure 6e and the y axis for all figures.**

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



**Line 490: Please give the rate coefficient for 2,2,3-trimethylpentane with 491 chlorine atoms.**

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

…such as the reaction of 2,2,3-trimethylpentane with chlorine atoms. It is currently known that the rate constant for the reaction of 2,2,3-trimethylpentane with OH radical at room temperature is $4.84\times10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, according to the above correlation equation, it can be inferred that the rate constant with chlorine atoms is $2.72\times10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$…

**Line 511: "11d"**

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

…..such as propane, the lifetime is 11 days….

**Line 520-522: please refine the conclusions after the modification performed from the reviewers suggestions**

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

The use of the multivariate relative rate method in this study allowed for the simultaneous determination of reaction rate coefficients of $C_3$-$C_{11}$ alkanes and OH radicals, which significantly improved the efficiency of determination. A total of 25 relative rate coefficients at room temperature were obtained, including the determination of a previously unreported room temperature relative rate coefficient for 3-methylheptane. For the studied n-alkanes, the obtained rate coefficients ($k_{OH}$) were found to be consistent with results estimated by the SAR methods using parameters provided by various positional groups, such as Atkinson and Kwok, Neeb, Wilson, Jenkin, and McGillen. However, it is important to note that parameters other than those provided by Wilson group do not appear to reasonably estimate the rate coefficients of

2,3-dimethylbutane. Additionally, SAR estimates for several cyclic alkanes (cyclopentane, methylcyclopentane, cyclohexane) and branched alkanes (2,2,4-trimethylpentane) appear to be overestimated compared to our measurements. This raises reasonable suspicion that these methods may still lack consideration of additional factors. Arrhenius expressions for the reaction of 2-Methylhepane and 3-Methylheptane with OH radicals were obtained for the first time in the temperature range of 273-323 K, expanding the existing database. In addition, correlation equations for the rate coefficients of alkanes reacting with OH radicals and chlorine atoms were obtained, and the rate coefficient of 2,2,3-trimethylpentane with chlorine atoms, which has not yet been reported, was deduced. The atmospheric lifetimes of the alkanes were also obtained for further prediction of their environmental impact.

**Line 523: there is no “structure-additivity method”**

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

…The method of structure-activity relationship for rate constant estimation is mostly consistent for the prediction of $k_{\mathrm{OH}}$ (298 K) for the studied n-alkanes,…

**RC2:**

**1.Major points:**

**Figure 5: There are many problems with this graph.**

**I am assuming that the black lines are Arrhenius fits. As discussed in your review, Arrhenius fits aren't very useful for this set of compounds over a large temperature range (for example, panel D shows just how poorly this approach describes the data), and I would recommend other fits such as k(T) = Aexp(B/T)(T/300)^n or k(T) = AT^n*exp(B/T), where A = A-factor, B = E/R and n = an additional term to provide curvature.**

**The units on the y-axes are wrong (cm^3 molecule^-1 s^-1).**

**There are missing data from the plots:**

**Panel A:**

**Anderson et al., 2004 (DOI: https://doi.org/10.1021/jp0472008); Behnke et al., 1988 (DOI: https://doi.org/10.1016/0004-6981(88)90341-1); Nolting et al., 1988 (DOI: https://doi.org/10.1007/BF00048331); Han et al., 2018 (DOI: https://doi.org/10.3390/atmos9080320); Ferrari et al., 1996 (DOI: https://doi.org/10.1002/(SICI)1097-4601(1996)28:8%3C609::AID-KIN6%3E3.0.CO;2-Z)**

**Panel B:**

**Sivaramakrishnan et al., 2009 (DOI: https://doi.org/10.1021/jp810987u); Pang et al., 2011 (DOI: https://doi.org/10.1524/zpch.2011.0156); Han et al., 2018 (DOI: https://doi.org/10.3390/atmos9080320)**

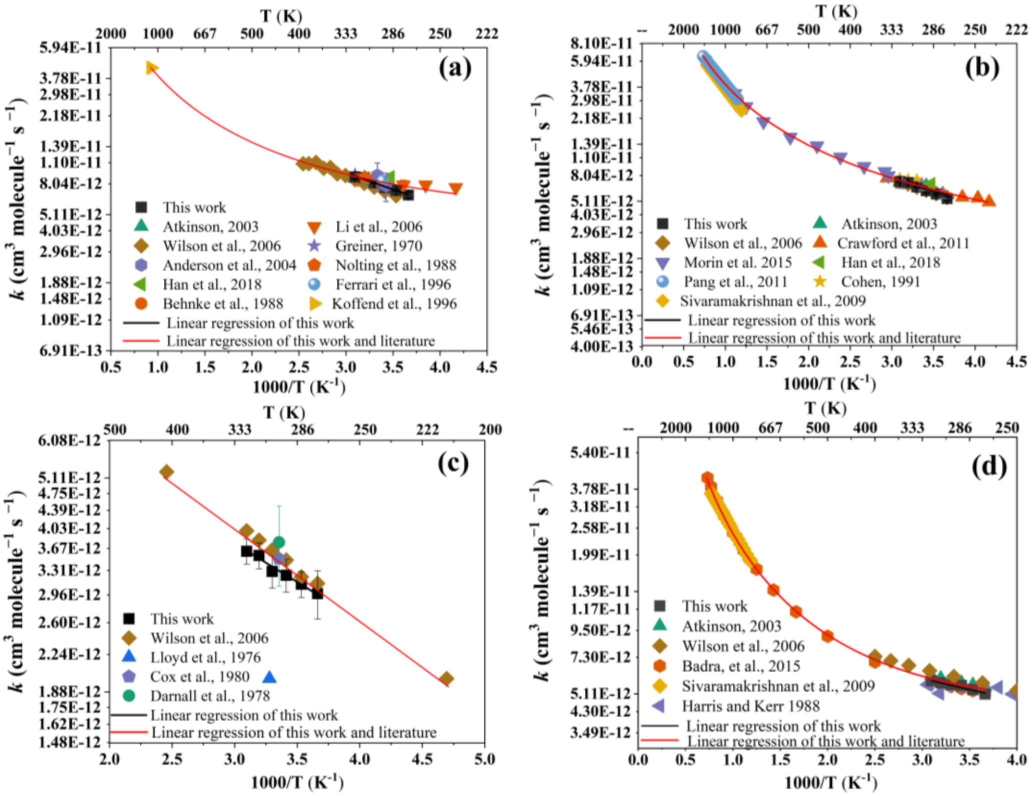
**Panel C:**

**Atkinson et al., 1984 (DOI: https://doi.org/10.1002/kin.550160413); Cox et al., 1980 (DOI: https://doi.org/10.1021/es60161a007); Darnall et al., 1978 (DOI: https://doi.org/10.1021/j100503a001); Lloyd et al., 1976 (DOI: https://doi.org/10.1021/j100549a003)**

**Panel D:**

**Harris and Kerr, 1988 (DOI: https://doi.org/10.1002/kin.550201203); Wilson et al., 2006 (DOI: https://doi.org/10.1021/jp055841c) Also, the work of Sivaramakrishnan et al., 2009 is conducted at high temperature and the other points don't seem to match up with the figure legend.**

**Reply:** Thanks for your valuable suggestions! In the article of Atkinson et al., 1984, **(DOI: https://doi.org/10.1002/kin.550160413)** there is no mention of isopentane, but only of isobutane. Modifications have been made in the revised manuscript.



## 2.Conclusions:

**The conclusions have not changed since the review. They should be updated to reflect the contents of the revised article (for example, it was already pointed out that your study does not present the first temperature-dependent data for methylcyclopentane, and yet, this is what you claim in your conclusions. This is unacceptable, this error has already been pointed out in your earlier review. Also, you have now applied several SAR methods for rate constant estimation, it would be useful to summarize the findings of these different methods.**

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

The use of the multivariate relative rate method in this study allowed for the simultaneous determination of reaction rate coefficients of $C_3$-$C_{11}$ alkanes and OH radicals, which significantly improved the efficiency of determination. A total of 25 relative rate coefficients at room temperature were obtained, including the determination of a previously unreported room temperature relative rate coefficient for

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

**Minor points:**

**Title:**

**The numbers 3 and 11 should be in subscript. This change should be applied throughout your manuscript (not just the title).**

**Reply:** Thanks for your valuable suggestions! All $C_3$-$C_{11}$ have been revised in the revised manuscript.

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

…Rate coefficients for the reactions of OH radicals with $C_3$-$C_{11}$ alkanes were determined using the multivariate relative rate technique…

…Anderson et al. obtained the $k_{OH}$ of $C_2$-$C_8$ several n-alkanes and…

**Abstract:**

**Line 16: the edit is worse than the original. I suggest to change it back to how it was.**

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

...A total of 25 relative rate coefficients at room temperature and 24 Arrhenius expressions in the temperature range of 273-323 K were obtained…

**Line 18: kOH. k should be italicized. OH shouldn't be italicized. The authors should carefully go through their manuscript and correct each instance of this problem.**

**Reply:** Thanks for your valuable suggestions! Modifications about all $k_{OH}$ have been made in the revised manuscript.

…The absolute rate method (such as flash photolysis and emission flow et al.) involves calculating the reaction kinetics parameter $k_{\mathrm{OH}}$ for organic compounds with OH radicals…

…Anderson et al. obtained the $k_{\mathrm{OH}}$ $C_2$-$C_8$ several n-alkanes and cyclic alkanes by the relative technique in the air system at 296 ± 4 K….

$k_{\mathrm{OH+n\text{-}Hexane}}=4.97\times10^{-12}$, $k_{\mathrm{OH+Cyclohexane}}=6.69\times10^{-12}$, $k_{\mathrm{OH+n\text{-}Octane}}=8.48\times10^{-12}$

…For example, the $k_{\mathrm{OH}}$ obtained for propane with n-hexane, cyclohexane and n-octane as the reference compound…

**Lines 20 – 26: The authors have employed several SAR methods now, and the results of these calculations should be included in your abstract.**

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

Interestingly, whilst results for n-alkanes agreed well with available structure activity relationship (SAR) calculations of Atkinson and Kwok, Neeb, Wilson, Jenkin, and McGillen, the three cyclo-alkanes (cyclopentane, methylcyclopentane, cyclohexane) and one branched alkane (2,2,4-trimethylpentane) were found to be less reactive than predicted by SAR. Conversely, the SAR estimates for 2,3-dimethylbutane were approximately 25 % lower than the experimental values, with the exception of those estimated by the Wilson group, highlighting the limited understanding of the oxidative chemistry of these compounds.

**Line 35: Remove the word "very".**

**Reply:** Thanks for your valuable suggestions! The "very" has been removed in the revised manuscript.

…The reactivity relation of saturated alkanes with OH radicals and chlorine atoms was obtained: $\log_{10}[k_{(\mathrm{Cl+alkanes})}] = 0.569\times\log_{10}[k_{(\mathrm{OH+alkanes})}]-3.111$ ($R^2$ =0.86)…

**Introduction:**

**Line 68: I am not familiar with the term "some secondary oxides". I recommend "oxygenated molecules".**

**Reply:** Thanks for your valuable suggestions! Combining your and other reviewer's suggestions, modifications have been made in the revised manuscript.

…Additionally, degradation products produced by the oxidation of alkanes can form…

**Lines 71 – 73: This is purely tautological. Essentially, you are stating that you need to measure how fast something reacts in order to evaluate how fast it reacts… Just delete these lines.**

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

…~~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)~~….

**Line 90: relies, not relied.**

**Reply:** I'm sorry for the mistake! Modifications have been made in the revised manuscript.

…the relative rate method relies on the recommended rate coefficient for the reaction of a reference…

**Line 98: "method" not "mehod".**

**Reply:** I'm sorry for the mistake! Modifications have been made in the revised manuscript.

…dozens of papers for the rate coefficients of alkanes with OH radical measured by relative rate method have been published…

**Methods:**

**Line 144: "$H_2O_2$ with respect to …".**

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

…$H_2O_2$ with respect to VOCs was injected through a three-way valve…

**Line 159: lower-case k for kd.**

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

…The $k_d$ values ranged from 1.3 to 4.8 (the units are $\times 10^{-4}$ ppbv/h)…

**Estimation of the rate constant at 298 K (SAR):**

**Mostly, this section has been improved, and I think the inclusion of the different methods is interesting. However, it was recommended by my review (referee 1) and that of referee 3 that you should try to compare with the recent SAR method of McGillen et al., 2024 (DOI: https://doi.org/10.1039/D3EA00147D). The reasons for this are that it is a distinctly different methodology to that of Atkinson, Wilson, Neeb, etc. The authors appear not to have been able to include these predictions. They are easy to do, and I list the results here:**

**I list the results here:**

**name k SAR**

**propane 1.20E-12**

**isobutane 2.17E-12**

**n-butane 2.38E-12**

**isopentane 3.37E-12**

**n-pentane 3.67E-12**

**cyclopentane 7.30E-12**

**2,2-dimethylbutane 1.94E-12**

**2,3-dimethylbutane 4.27E-12**

**2-methylpentane 4.65E-12**

**3-methylpentane 4.67E-12**

**methylcyclopentane 8.34E-12**

**2,4-dimethylpentane 5.56E-12**

**cyclohexane 8.76E-12**

**2-methylhexane 5.97E-12**

**3-methylhexane 6.00E-12**

**2,2,4-trimethylpentane 4.10E-12**

**n-heptane 6.40E-12**

**methylcyclohexane 9.76E-12**

**2,3,4-trimethylpentane 6.39E-12**

**2-methylheptane 7.34E-12**

**3-methylheptane 7.36E-12**

**n-octane 7.80E-12**

**n-nonane 9.21E-12**

**n-decane 1.06E-11**

**n-undecane 1.21E-11**

**I recommend that you include these new predictions in this section so that you can make a more complete comparison of the available SAR methods, and to discuss whether or not accounting for the cycle size is a useful parameter in these SARs. Also, why don't you compare the SAR estimates at different temperatures?**

**Reply:** Thanks for your valuable suggestions and help, it will help me a lot!

Modifications have been made in the revised manuscript.

In addition, there are a number of SAR methods that are quite different in their estimation from those of Atkinson, Wilson, et al. and Neeb, et al., for instance, the method of McGillen et al. Figure S3 shows a comparison of our measurements with the SAR estimates of McGillen et al. Similar to the results of Kwok and Atkinson, Neeb, and Jenkin et al., the obtained $k_{OH}$ values of cyclopentane and 2,3-Dimethylbutane in this study exceed the shaded area. This further illustrates that there is still a large discrepancy between the experimental values and the SAR estimates for both substances. For cycloalkanes, the SAR estimates of McGillen et al. are still overestimated to varying degrees compared to our measurements, especially for cyclopentane, where the experimentally measured $k_{OH}$ in this work is still about 34% lower than the SAR estimate. And the $k_{OH}$ values for cyclohexane, methylcyclopentane and methylcyclohexane were also lower than the estimated values by about 18%, 12% and 5%, respectively. For the branched alkanes, again the $k_{OH}$ of 2,3-Dimethylbutane is higher than the SAR estimate by about 32% or so. Similarly to the comparison with the Neeb, and Jenkin et al SAR estimates, the experimental measurements we obtained for 2,2,4-Trimethylpentane are also lower than the McGillen et al estimates by about 14%. By comparing the reaction rate coefficients of cyclopentane and cyclohexane, it is found that for cyclic alkanes of Kwok and Atkinson, Neeb, Jenkin et al., and McGillen et al, the cycle size increases by about$1.41\times10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$. However, For the SAR estimate of Wilson et al, the cycle size increases by about $1.12\times10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$.

Jenkin et al. obtained optimised Arrhenius parameters ($k$ =Aexp(−(E/R)/T)) for the group rate coefficients for H-atom abstraction from $-CH_3$, $-CH_2-$ and CH< groups of alkanes by SAR method, from this it is possible to derive reaction rate constants for different temperatures.

$k_{prim}=2.9\times10^{-12}\times\exp(-(925)/T)$

$k_{sec}=4.95\times10^{-12}\times\exp(-(555)/T)$

$F(-CH_3)=1$; $F(-CH_2-)= \exp(89/T)$

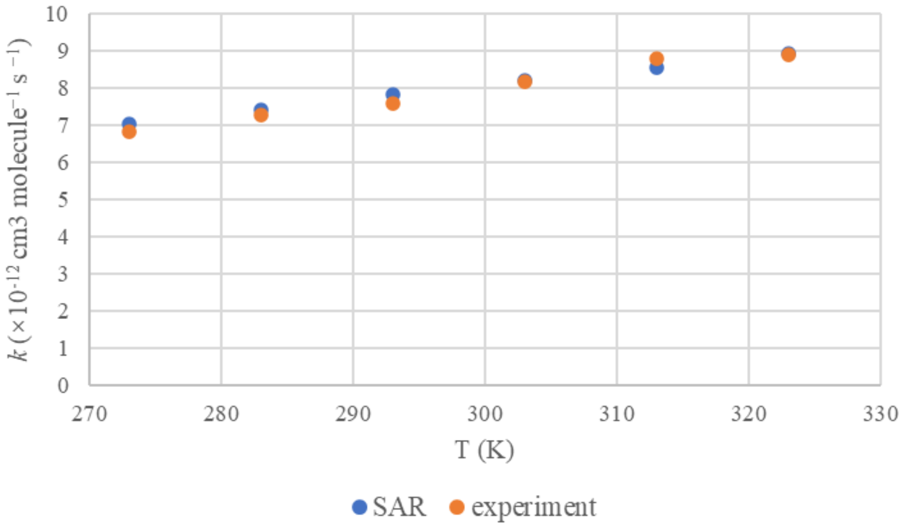
Take n-Octane e as an example:

(1) $k_{\mathrm{prim}} \times \mathrm{F(\text{-}CH_2\text{-})} \times 2 = 2.9\times10^{-12}\times\exp(-(925)/T)\times\exp(89/T)\times2$

(2) $k_{\mathrm{sec}} \times \mathrm{F(\text{-}CH_3)} \times \mathrm{F(\text{-}CH_2\text{-})} \times 2 + k_{\mathrm{sec}} \times \mathrm{F(\text{-}CH_2\text{-})}^2 \times 4 = 4.95\times10^{-12}\times\exp(-(555)/T)\times1\times$

$\exp(89/T)\times2+4.95\times10^{-12}\times\exp(-(555)/T)\ [\exp(89/T)]^2\times4$

Therefore, the comparison between the estimated values of the SAR method and the experimental values of the present work at different temperatures is shown in the following figure:



SAR estimates are in good agreement with the experimental values for n-octane at different temperatures. In addition, the experimental values of the other components at different temperatures within the error range are in good agreement with the SAR estimates. We added supplement for different temperatures in the revised manuscript.

**Line 448:** Also, the experimental values of n-Octane obtained at different temperatures are in high agreement with the SAR estimates.

**Line 269 (and everywhere else): k SHOULD NOT BE UPPER-CASE!**

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

…$k^0_{\mathrm{prim}}$ , $k^0_{\mathrm{sec}}$ , $k^0_{\mathrm{tert}}$ represent the rate coefficients of each -$CH_3$,…

…Atkinson and Kwok et al derived the values of $k^0_{\mathrm{prim}}$, $k^0_{\mathrm{sec}}$, $k^0_{\mathrm{tert}}$ at room temperature,

$k^0_{prim}$=0.136×$10^{-12}$, $k^0_{sec}$=0.934×$10^{-12}$, $k^0_{tert}$=1.94×$10^{-12}$, the unit is $cm^3$ $molecule^{-1}$ $s^{-1}$…

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

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

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

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

**Line 271: “update” not “updated”. “modify” not “modified”.**

**Reply:** I'm sorry for the mistake! Modifications have been made in the revised manuscript.

…many researchers continued to update and modify some parameters based on…

**Line 272: It is not clear what is meant by fundamental rate constant. Maybe chose “base rate constant” or something like this.**

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

…and obtained the new base rate coefficients for different positional groups,…

**Results and discussion:**

**Line 307: There is no such thing as a second-order C-H bond. You mean “secondary” perhaps.**

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

…reflects the fact that the main way is to extract the H atom from the secondary C-H bond…

**Line 311: “reactivity increases” not “reactivity increase”.**

**Reply:** I'm sorry for the mistake! Modifications have been made in the revised manuscript.

…can also be seen that the reactivity increases with the increase of cycle size…

**Table 1: This table is mostly OK, but I find it confusing that you have a column entitled "reference" (which should not be confused with your reference rate constant). I suggest to rename this column to "Literature measurements".**

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

| | | **This work** | | | **Literature measurements** |
|---|---|---|---|---|---|
| **Alkanes** | **Reference** | **$k_{OH}/k_{reference}$ ±1σ** | **$k_{OH}$ ±1σ ($\times10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$)** | **$k_{OH\text{-}av}$$^a$ ±1σ ($\times10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$)** | **$k_{OH}$ ($\times10^{-12}$cm$^3$ molecule$^{-1}$ s$^{-1}$)** |
| Propane | n-Hexane | 0.190±0.033 | (9.43±1.66) | (1.01±0.26) | 1.11 $^{bcd}$<br>1.09 $^e$<br>1.91 $^f$<br>(1.15±0.15) $^g$ |
| | Cyclohexane | 0.153±0.028 | (1.03±0.18) | | |
| | n-Octane | 0.136±0.031 | (1.16±0.26) | | |

**Comparisons to structure-activity relationships:**

**Lines 453 – 455: Under the circumstances of this study, I find it strange that you would evaluate the reliability of experimental data by comparing with SAR estimates. If conducted well, an experimental measurement will be considerably more reliable than an estimation technique. Therefore, rather than assessing how reliable the experiment is, more realistically, this comparison assesses how accurate the estimation technique is.**

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

To assess the accuracy of the estimation technique, multiple comparisons were made between the obtained reaction rate coefficients and the SAR…

**Line 462: "branched" not "branch".**

**Reply:** I'm sorry for the mistake! Modifications have been made in the revised manuscript.

….For branched alkanes, such as monomethyl branched alkanes….

**Line 464: what is "shadow range"? The meaning is unclear, rephrase.**

**Reply:** I'm sorry for the mistake! Modifications have been made in the revised manuscript.

….the obtained $k_{OH}$ values all fall within the shadow area…

**Line 497: "n-nonane"**

**Reply:** I'm sorry for the mistake! Modifications have been made in the revised manuscript.

(23) n-nonane;

**Temperature dependence (273-323 K):**

**Table 2: similar to Table 1, I suggest to rename this column "Reference" to "Literature measurements".**

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

| **Alkanes** | **Temperature (K)** | **A-factor $^a$ ($\times 10^{-11}$)** | **$E_a/R^b$ (K)** | **Technique $^c$** | **Literature measurements** |
|---|---|---|---|---|---|
| Propane | 273-323 | 2.38±0.90 | 952±110 | RR/DP/GC-FID | this work |
| | 296-908 | 2.71±0.17 | 988±31 | AR/FP/LIF | (Bryukov et al., 2004) |
| | 227-428 | 1.29 | 730 | RR/DP/GC | (Demore and Bayes, 1999) |
| | 233-376 | 1.01 | 660 | AR/FP/LIF | (Talukdar et al., 1994) |

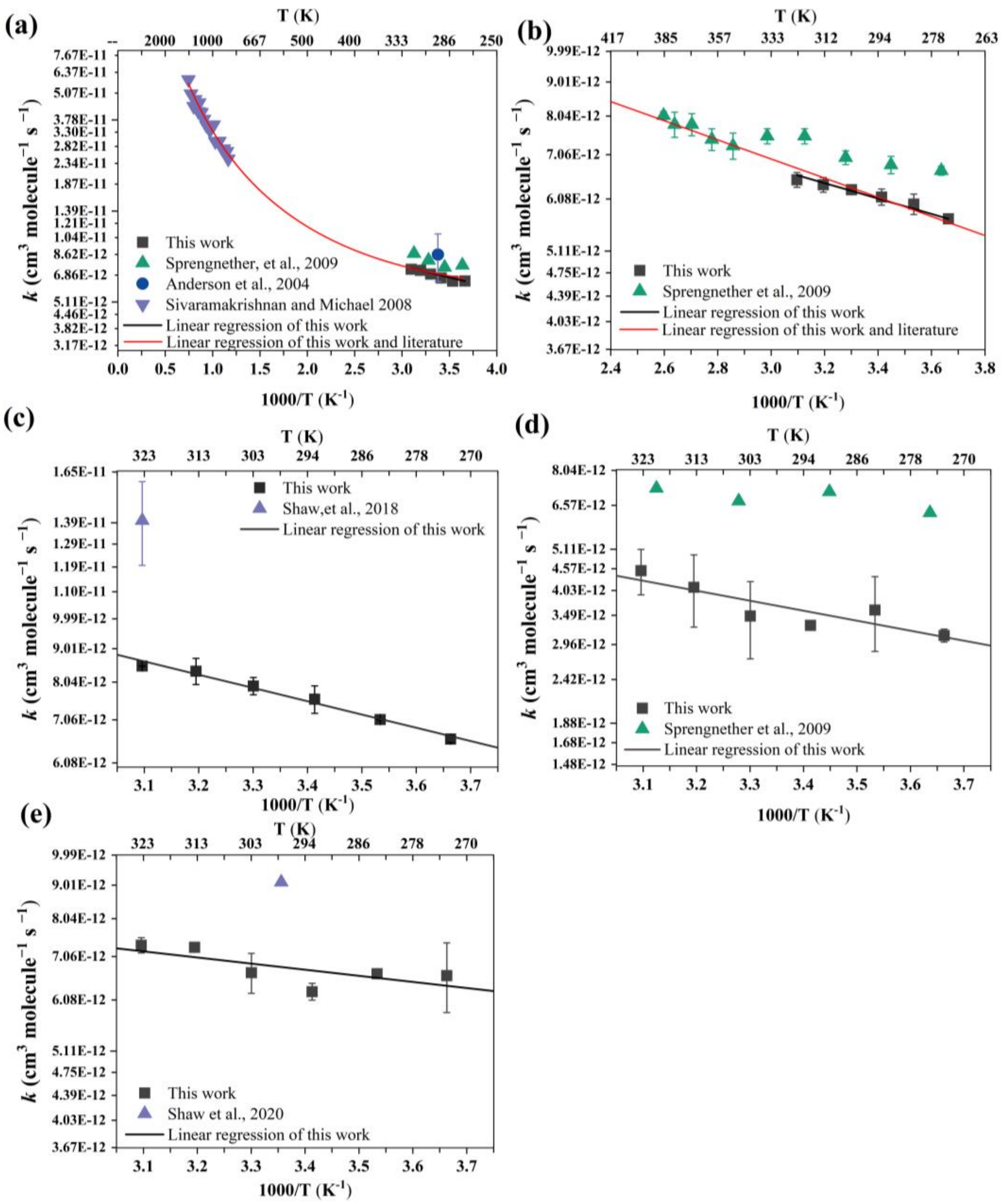
**Figure 6: Similar to Figure 5, there are several errors here. Figure caption contains misspellings of 3-methylheptane and 2-methylheptane.**

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

Figure 6. Arrhenius plots for the reaction of Methylcyclopentane (a), 2-Methylhexane (b), 3-Methylheptane (c), 3-Methylhexane (d) and 2-Methylheptane (e) with OH radical along with available literature data…

**Panel A: The work of Anderson was conducted at 296 K. The high temperature measurements were conducted by Sivaramakrishnan and Michael, 2008 (so your legend is incorrect).**

**Reply:** I'm sorry for the mistake! Modifications have been made in the revised manuscript.



**Correlation between the rate coefficients of the reaction of alkanes with OH 672 radicals and chlorine atoms:**

**Line 677: replace “discrete” with “weak”?**

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

…Although the correlation between propane and isobutane is relatively weak, the reactivity of…

**Atmospheric lifetime and implications:**

**Lines 693 – 694: The reference Li et al., 2018 did not assess the atmospheric**

**abundance of OH radicals. Choose a relevant reference for this point.**

**Reply:** I'm sorry for the mistake! Modifications have been made in the revised manuscript.

Lawrence, M. G., Jöckel, P., and von Kuhlmann, R.: What does the global mean OH concentration tell us?, Atmospheric Chemistry and Physics, 1, 37-49, https://doi.org/10.5194/acp-1-37-2001, 2001.

**Line 696: "in" not "on the". "lifetimes" not "lifetime".**

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

… As can be seen from the table, the atmospheric lifetimes of $C_3$-$C_{11}$ alkanes reacting with OH radicals are about 1-11 days…

**Line 698: "lifetimes are reduced" not "lifetime seems to reduce".**

**Reply:** I'm sorry for the mistake! Modifications have been made in the revised manuscript.

…As the carbon chain grows, the atmospheric lifetimes are reduced, especially…

**Lines 701 – 702: $RO_2$ will serve to convert NO to $NO_2$ directly. The role of $HO_2$ is also important, but is not directly related to the peroxy radicals mention here.**

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

…They are emitted into the air and degraded quickly to generate alkyl radicals, which are immediately converted into alkyl peroxy radicals by reacting with abundant $O_2$ in the atmosphere. Alkyl peroxyl radicals will serve to convert NO to $NO_2$ directly, leading to the production of tropospheric ozone….

**Line 703: 11 days is not a "long time".**

**Reply:** Thanks for your valuable suggestions! I sincerely apologize that the expression is not accurate enough here. Modifications have been made in the revised manuscript.

…Longer atmospheric residence time of short-chain alkanes compared to long-chain C8-C11 alkanes, such as propane…

**Lines 703 – 705: This is tautological in its present form, and should be removed.**

**Reply:** Thanks for your valuable suggestions! The tautological portions have been removed in the revised manuscript.

~~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.~~

**Line 710: previous temperature dependent data exists for methylcyclopentane. You must change this accordingly.**

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

…Arrhenius expressions for the reaction of 2-Methylhepane and 3-Methylheptane with OH radicals were obtained for the first time in the temperature range of 273-323 K,….

**Lines 716 – 717: is this true of all SAR techniques or just one of them?**

**Reply:** Thank you very much for your query, which is addressed here for the above 4 SAR techniques and the conclusions have been modified for a clearer summary.

**Line 720: More than one method has been employed. The use of the singular "method" is inappropriate and should be updated.**

**Reply:** I'm sorry for the mistake! Modifications have been made in the revised manuscript.

…This raises reasonable suspicion that these methods may still lack consideration of additional factors.

RC3:

**1. Minor: It is highly recommended the authors to preferably use rate coefficient instead of rate constant. k is not a constant - although the term is used in the literature - and they have clearly described that depends on T! This comment was also present in the first review.**

**Reply:** Apologies for not being able to complete all the changes to rate constant in the last revision! All rate constant has been replaced with rate coefficient in the revised manuscript.

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

…By monitoring the simultaneous decay of the target and reference compounds in the presence of OH radicals due to competitive response mechanisms, the rate coefficient for the reaction of OH radicals with the target compound….

**2. Major: In absolute and relative rate methods comparison the authors should be very careful! They use the term known, although they should use the term recommended. The fact that a reaction rate cofficient has been measured doesn't mean that is known! It deppends on them whst k-values they would use for their reference reaction used, but they need to justify why they used those. It is strongly recommended to use the evalusted rate coefficients values from NASA/JPL and IUPAC panels, where exist and if not they need to do their own evaluation and justify their selection. Please keep in mind that absolute rate coefficients determinations although sometimes might be more demanding and challenging do not rely on other measurements and thus are not subzected on systematic errors of previous measurements, that are larger at temperatures away from room temperature. Particularly when so many reaction rate coefficients are measured at once it is very likely that reaction products etc might interfere in their subtraction analysis and the error bars that should be quoted cannot be less than 15 %. Like mentioned in the previous review, the error analysis of the kinetic data presented in this work is actually missing! What are the estimated systematic**

**uncertainties of authors measurements? How they have been estimated?**

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

(1) …Unlike the absolute rate method, the relative rate method relied on the recommended rate coefficie for the reaction of a reference…(Line 60)

(2) …The basic principle is that the rate coefficient for the reaction of the reactant used as a reference with OH radicals needs to be the recommended rate coefficients values, (Line 137)

(3) The rate constant of the reference compound we used was not found in the NASA/JPL and IUPAC database, so we chose the expert evaluated data from McGillen et al.

(4) The ratio $k/k_{ref}$ is derived from ln–ln plots. The error, σ, is calculated as the standard error based on the product of $k/k_{ref}$ obtained in several experiments and the $k_{ref}$ recommended in the literature.

The derived rate coefficients are weighted average of the obtained data with various references taking into account of the uncertainties on the references rate coefficients values as: $k_{av} = (w_{ref1} k_{ref1} + w_{ref2} k_{ref2} + \ldots)/ (w_{ref1} + w_{ref2} + \ldots)$, where $w_{ref1} = 1/\sigma_{ref1}^{2}$, etc. The error, $\sigma_{av}$, was given by: $\sigma_{av} = (1/\sigma_{ref1} + 1/\sigma_{ref2} + \ldots)^{-0.5}$ (Farrugia et al., 2015): unit of $cm^3$ $molecule^{-1}$ $s^{-1}$.

**3. Major: Figure 5: (a) First please use the same symbols in all 4 plots when you refer to the same literature study, for consistency purposes. For instance, for Atkinson et al. (2003) you have used three different symbols and colors, which makes the comparison confusing for the reader. (b) Include temperature as mirror to bottom axis, so as the reader to have a direct access to the temperature that the kinetic data refer to just lookin the plot. (c) do the 2σ error bars include systematic uncertainties? How the error bars shown in figure 5c, for instance, were determined? Why the error bar at 273 K is that smaller compared to 296 K and then becomesd that smaller again at 313 K? Systematic uncertainties normally**

**become larger away from room temperature, where most of the test measurements are carried out. This plot doesn't seem to include the systematic uncertainties from the reference reactions or they have mistakenly included. If this is tonly the 2σ precision of the fits, why the present measurements have so large error limits? (d) What are the fits shown in all 4 plots. First they do not fit the data! Why the authors didn't try to fit the actual data with a modified Arrhrnius expression? To present fits that are not representing this work or combined with literature measured data seems odd. The easiest way around it is to fit their data and discuss the agrrement with other literature data in the same temperature data. The k(T)-trends observed in these plots might contain important mechanistic information that the authors have disregarded!**

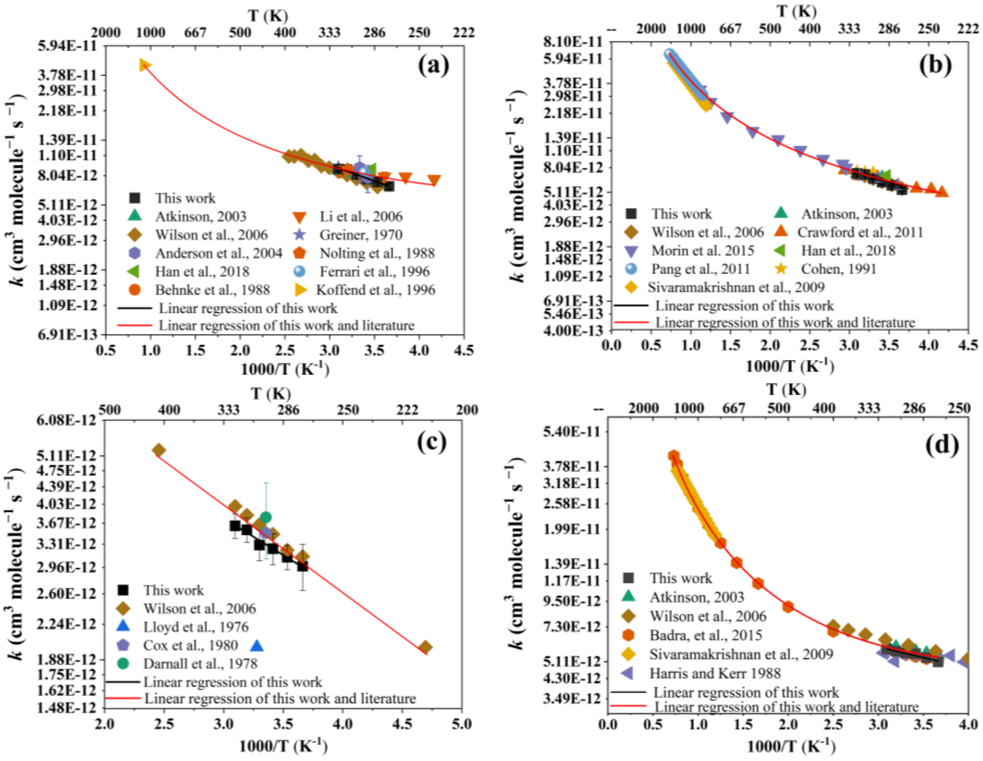
**Reply:** Thanks for your valuable suggestions! Modifications have been made in the revised manuscript.

**(a)** All the symbols and colours in all 4 plots have been harmonized in the revised manuscript.

**(b)** Temperature is added as a mirror image of the bottom axis in the figure.

**(c)** 2σ in the figure is the error for each temperature, which is calculated as the standard error based on the product of $k/k_{\mathrm{ref}}$ obtained in several experiments and the $k_{\mathrm{ref}}$ recommended in the literature. In addition, we returned to the original spectrogram and reprocessed the data, the corrected data are shown in Figure 5(c).

**(d)** We obtained the Arrhenius expression for the range 273-323 K by performing experiments in the temperature range under study (273-323 K). In addition we fitted again to the high temperature data from the literature based on the comments of other reviewers, assigning curvature to the data as it varied and fitting it with a new expression ($k(T) = A*\exp(B/T)*(T/300)^n$) to obtain the actual expression.


(a)
T (K)
2000 1000 667 500 400 333 286 250 222
k (cm$^3$ molecule$^{-1}$ s$^{-1}$)
5.94E-11 3.78E-11 2.98E-11 2.18E-11 1.39E-11 1.10E-11 8.04E-12 5.11E-12 4.03E-12 2.96E-12 1.88E-12 1.48E-12 1.09E-12 6.91E-13
1000/T (K$^{-1}$)
0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5
This work
Atkinson, 2003
Wilson et al., 2006
Anderson et al., 2004
Han et al., 2018
Behnke et al., 1988
Li et al., 2006
Greiner, 1970
Nolting et al., 1988
Ferrari et al., 1996
Koffend et al., 1996
Linear regression of this work
Linear regression of this work and literature
(b)
T (K)
-- 2000 1000 667 500 400 333 286 250 222
k (cm$^3$ molecule$^{-1}$ s$^{-1}$)
8.10E-11 5.94E-11 3.78E-11 2.98E-11 2.18E-11 1.39E-11 1.10E-11 8.04E-12 5.11E-12 4.03E-12 2.96E-12 1.88E-12 1.48E-12 1.09E-12 6.91E-13 5.46E-13 4.00E-13
1000/T (K$^{-1}$)
0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5
This work
Wilson et al., 2006
Morin et al. 2015
Pang et al., 2011
Sivaramakrishnan et al., 2009
Atkinson, 2003
Crawford et al., 2011
Han et al., 2018
Cohen, 1991
Linear regression of this work
Linear regression of this work and literature
(c)
T (K)
500 400 333 286 250 222 200
k (cm$^3$ molecule$^{-1}$ s$^{-1}$)
6.08E-12 5.11E-12 4.75E-12 4.39E-12 4.03E-12 3.67E-12 3.31E-12 2.96E-12 2.60E-12 2.24E-12 1.88E-12 1.75E-12 1.62E-12 1.48E-12
1000/T (K$^{-1}$)
2.0 2.5 3.0 3.5 4.0 4.5 5.0
This work
Wilson et al., 2006
Lloyd et al., 1976
Cox et al., 1980
Darnall et al., 1978
Linear regression of this work
Linear regression of this work and literature
(d)
T (K)
-- 2000 1000 667 500 400 333 286 250
k (cm$^3$ molecule$^{-1}$ s$^{-1}$)
5.40E-11 3.78E-11 3.18E-11 2.58E-11 1.99E-11 1.39E-11 1.17E-11 9.50E-12 7.30E-12 5.11E-12 4.30E-12 3.49E-12
1000/T (K$^{-1}$)
0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0
This work
Atkinson, 2003
Wilson et al., 2006
Badra, et al., 2015
Sivaramakrishnan et al., 2009
Harris and Kerr 1988
Linear regression of this work
Linear regression of this work and literature