

Interactive comment on “Experimental and computational kinetics investigations for the reactions of Cl atoms with unsaturated ketones in gas phase” by Siripina Vijayakumar *et al.*

We thank the reviewer for going through the manuscript entitled “**Experimental and computational kinetics investigations for the reactions of Cl atoms with unsaturated ketones in gas phase**” and for his/her constructive suggestions to improve the quality of the manuscript. We have incorporated all the suggestions and given explanations to the queries in the revised manuscript (RMS) at appropriate places. The changes/additions in the revised manuscript are given in blue color for ready reference. The complete rebuttal is given below.

Anonymous Referee #1

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General Comments: Authors have reported experimental and computational studies on gas phase reaction kinetic of Cl atom + unsaturated ketones. These species have been detected in the atmosphere. The paper describes experimental and computational rate coefficients, which can be helpful to understand the reactions mechanism of unsaturated ketones initiated by Cl radical. The theoretical and experimental rate coefficients were compared with data available in the literature. It is an interesting paper. This paper is publishable after minor revisions noted.

Specific Comments:

The unsaturated ketones 4-hexen-3-one, 5-hexene-2-one and 3-penten-2-one have E and Z isomers. I don't see any discussions on their isomers. Neglecting these isomers may lead error in the computational k, which is near about factor of 2 at room temperature. May be Hindered rotor treatment can solve the discrepancy of the computational rate with the reference rate (experimental). I can see in Figure 2, the rate coefficients agree within 50% with the reference value and previously measured value. However, the calculated rate coefficient at the lower temperature (275K) is near about a factor of 10 and at the higher temperature (400K), it is 100 lower than the experimental value. In my experience, this problem could be due to HR treatment

and neglecting the other isomer. Another way to improve the calculations is to check MP2 imaginary frequencies. These errors are related to pre-exponential factor.

A little adjustment of barrier heights may be gives you closer value in the entire temperature range. You can find the error in the energy calculation based previous papers J. Phys. Chem. A 2015, 119, 7578–7592 and J. Phys. Chem. A 2016, 120,7060–7070. You can discuss your results similar way and cite these papers.

Response: In both 4-hexen-3-one and 3-penten-2-one one methyl group is attached at the terminal carbon of the double bond. Therefore, E (trans) and Z (cis) isomers exist for both the compounds. Whereas, in case of 5-hexen-2-one, the double bond is connected to three hydrogens (two at the terminal carbon and one at the other end of the double bond) and therefore it exists as a single conformer only. We tried to optimize both trans and cis isomers of the first two systems. However, we could not optimize the cis isomers, probably as they are highly unstable. Under these circumstances, we have considered the most stable trans isomer in our calculations.

Hindered rotor (HR) calculations were performed and compared with the present experimental and reported rate coefficients (given below). Rate coefficients obtained including HR corrections are almost equal to our earlier theoretical calculations. As the reviewer rightly pointed, the discrepancy between theoretical and the present experimental rate coefficients may be due to the errors in pre-exponential factors and the errors in the estimation of barrier heights. As the rate coefficient at a given temperature is the combination of both pre-exponential factor and the activation energy, the difference can be attributed to the accuracy with which both these factors are determined. The pre-exponential factor depends on how best the partition functions of reactants and transition states are estimated, which in turn depends on the vibrational frequencies obtained in the calculations. On another hand, the uncertainties in the calculated energies of transition states can critically affect the calculated rate coefficients. Lynch *et al.*, 2001; Ali *et al.*, 2016; and Ali *et al.*, 2015 concluded that, there would be an error of about 1.1 kcal mol⁻¹ in the barrier height calculations at the CCSD(T) level of theory with 6-31+G(d,p) basis set. The same level of theory and the basis set were used in the present calculations. Therefore, given an uncertainty of about 1 kcal mol⁻¹ in the activation barrier, the theoretically calculated rate coefficients are in reasonable agreement with the reported experimentally measured ones. This discussion is added in the RMS.

Table: Comparison of the rate coefficients ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for the reactions of unsaturated ketones with Cl atoms at 298K.

	4-hexen-3-one + Cl	5-hexen-2-one + Cl	3-penten-2-one + Cl
k_{Theory}	3.66×10^{-10}	5.56×10^{-10}	2.4×10^{-10}
$k_{\text{Theory with HRcorrection}}$	3.60×10^{-10}	5.47×10^{-10}	2.38×10^{-10}
$k_{\text{Experimental}}$	$(5.55 \pm 1.31) \times 10^{-10}$	$(4.14 \pm 1.25) \times 10^{-10}$	-
$k_{\text{Blanco et al.}}$	$(3.00 \pm 0.58) \times 10^{-10}$	$(3.15 \pm 0.50) \times 10^{-10}$	$(2.53 \pm 0.54) \times 10^{-10}$

Table: Comparison of the theoretically obtained rate coefficients ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for the reaction of Cl atoms with unsaturated ketones at CCSD(T)/6-31+G(d, p)//MP2/6-311++G (d, p) level of theory over the temperature range of 275-400K.

	4-hexen-3-one + Cl		5-hexen-2-one + Cl		3-penten-2-one + Cl	
T (K)	k_{Theory}	$k_{\text{Theory with HRcorrection}}$	k_{Theory}	$k_{\text{Theory with HRcorrection}}$	k_{Theory}	$k_{\text{Theory with HRcorrection}}$
275	5.81×10^{-10}	5.73×10^{-10}	1.09×10^{-09}	1.07×10^{-09}	3.51×10^{-10}	3.48×10^{-10}
298	3.66×10^{-10}	3.60×10^{-10}	5.56×10^{-10}	5.47×10^{-10}	2.40×10^{-10}	2.38×10^{-10}
325	2.33×10^{-10}	2.29×10^{-10}	3.85×10^{-10}	3.78×10^{-10}	1.66×10^{-10}	1.65×10^{-10}
350	1.64×10^{-10}	1.62×10^{-10}	2.44×10^{-10}	2.40×10^{-10}	1.26×10^{-10}	1.24×10^{-10}
375	1.22×10^{-10}	1.20×10^{-10}	1.57×10^{-10}	1.54×10^{-10}	9.89×10^{-11}	9.79×10^{-11}
400	9.49×10^{-11}	9.35×10^{-11}	1.00×10^{-10}	9.83×10^{-11}	8.07×10^{-11}	7.99×10^{-11}

Lynch, B. J. and Truhlar, D. G.: How well can hybrid density functional methods predict transition state geometries and barrier heights? J. Phys. Chem. A 105, 2936-2941, 2001.

Ali, M. A., Sonk, J. A. and Barker, J. R.: Predicted chemical activation rate constants for $\text{HO}_2 + \text{CH}_2\text{NH}$: The dominant role of a hydrogen bonded pre-reactive complex. J. Phys. Chem. A 120, 7060-7070, 2016.

Ali, M.A. and Barker, J.R.: Comparison of there isoelectronic multiple-well reaction systems: $\text{OH} + \text{CH}_2\text{O}$, $\text{OH} + \text{CH}_2\text{CH}_2$, and $\text{OH} + \text{CH}_2\text{NH}$. J. Phys. Chem. A 119, 7578-7592, 2015.

Minor Comments:

Abstract No need to write a full description of Arrhenius expressions. May be something like $k_1 = \text{---}$, $k_2 = \text{---}$ will work.

Response: It was corrected and Arrhenius expressions are written as $k_1 = (2.82 \pm 1.76) \times 10^{-12} \exp[(1556 \pm 438)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_2 = (4.6 \pm 2.4) \times 10^{-11} \exp[(646 \pm 171)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in the RMS.

Introduction: Page 1 Line 2: I think hydrocarbon should be written as an Organic Compounds. Hydrocarbon contains only hydrogen and carbon. Line 5-7: Need citations.

Response: hydrocarbons word is replaced with organic compounds. The following reference is cited for lines 5-7 in the RMS.

Seinfeld, J. H. and Pandis, S. N.: Atmospheric Chemistry and Physics: From Air Pollution to Climate Change; John Wiley & Sons: New York, 1997.

Line 17-19: these ketones, please be specific.

Response: ketones are specified in RMS and they are acetone, 2-butanone, 3-pentanone and 2-pentanone.

Page 5 line 11: Why rate expression is in the bold letter? Need equation number.

Response: Bold fonts are now replaced with regular fonts and all equations are numbered in the RMS.

Computational Methodology Page 1 Line 1: MP2 calculations are based on full electrons or based on frozen cores?

Response: These MP2 calculations are based on frozen cores.

Page 1 line 3: What are the reactive complexes (RCs)? I think it should be PRC (Pre-reactive Complex).

Response: They are Pre-reactive Complexes (PRCs) and corrected in RMS.

Page 1 line 5: IRC calculation at MP2 level for what reason?

Response: Intrinsic Reaction Coordinates (IRCs) calculations were performed to check the transition states are connected to reactant and products. Also, to find if all the reaction pathways are independent of each other. This is added in the computational methodology of the RMS.

Results and Discussion Page 7 Line 3: “May be this is due to the differences in the rate coefficients of the reference compounds and uncertainties associated with the reference compounds which were used in the present measurements. This statement confused me, whether your measured rate coefficients are correct or computational rate coefficients? Need modifications.

Response: The above sentence is modified as “The difference between the present experimental and reported rate coefficient, may be due to the differences in the rate coefficients of the reference compounds and associated uncertainties, which were used in the present measurements” in the RMS.

Figure 3: For H- atom, I think, white or gray color is appropriate. I think Blue color represent N atoms.

Response: The standard colors for ‘C’ atom - gray color, ‘H’ atom –white color, ‘O’ atom- red color and ‘Cl’ atom – green color are used in the RMS.

Figure 3: TS1 and TS2a should be corrected as discussed in Page 8 in structure 1: 4-hexen-3-one.

Response: Addition transition states are represented by TS1a (adjacent to the CH₃ group) and TS2a (adjacent to the C=O group) as shown in the structure 1: 4-hexen-3-one in the RMS.

Figure 6. PES is incomplete; I don’t see the PRC energy. I guess the Electronic + ZPE is calculated. Not sure that if authors have included thermal corrections?

Response: We have incorporated PRCs with energies in Figure 6 (PES) in the RMS. We have taken the sum of electronic and zero-point energies. We have not included thermal corrections.

Page 9: I think Products P1a and P2a should be corrected as Intermediates or Adults.

Response: As the products P1a and P2a are alkyl radicals, we have renamed as intermediates in the RMS as given below.

“The Cl atom addition on double bond at TS1a and TS2a lead to the formation of intermediates P1a and P2a respectively”.

Page 9: Why not comparing your theoretical value to your experimentally measured value for all three cases in the same place where you compare with Blanco et al.

Response: We have reorganized experimental and theoretical sections in the RMS, which gives the better continuity and explain all three systems in the same place.

Figure 7 and 9: Structure of RC2a is missing. If RC1a and RC2a are structurally and energetically same, then why two different pre-reactive complexes?

Response: In Figure 7 and 9, structures of RC1a and RC2a are energetically same but their structures are different. The Cl atom addition at TS1a and TS2a leads to the formation of pre-reactive complexes via PRC1a and PRC2a respectively and these structures are given in the RMS.

Page 11: Again this statement should be corrected “May be this is due to the uncertainties associated with the submerged transition states. I don’t think submerged TS can underestimate or overestimate the k. May be problem-related to and theoretically calculated pre-exponential factors or calculated energies using at MP2 level. Please refer to my earlier comments.

Response: We have modified the above sentence as “the discrepancy between theoretical and the present experimental rate coefficient may be due to the errors in pre-exponential factors and the errors in the estimation of barrier heights. As the rate coefficient at a given temperature is the combination of both pre-exponential factor and the activation energy, the difference can be attributed to the accuracy with which both these factors are determined. The pre-exponential factor depends on how best the partition functions of reactants and transition states are estimated which in turn depends on the vibrational frequencies obtained in the calculations.” This discussion is added in the RMS.

I don’t think the value reported -3.80 and -3.45 kcal/mol are the barrier heights for addition reactions. Check it.

Response: For the reaction of Cl atom with 4-hexen-3-one, the relative energy barrier heights for TS1a and TS2a are -3.80 and -3.45 kcal mol⁻¹ are correct and given in Table 6 of the RMS.

Table 9: Something wrong with title or table contents.

Response: In Table 9, we have compared the rate coefficients for the reactions of unsaturated ketones with OH radicals, Cl atoms and NO₃ radicals. The title of the table is modified as

“Comparison of the rate coefficients for the reactions of unsaturated ketones with Cl atoms, OH and NO₃ radicals at 298K” in the RMS.

Conclusions:

Authors stated in the conclusion “As these molecules are short-lived they would not contribute to global warming in any time horizons.” Then why there are performing the measurement and calculations? Some benefit should be added. Also, why reporting lifetimes at 298K.

Response: The cumulative lifetimes of the studied molecules are estimated to be an hour and global warming potential of these molecules are negligible (0.01). When these molecules are released into the atmosphere, within an hour they are lost from its original form. And also, we have calculated ozone formation potentials in the troposphere for the title reactions, which are 7, 6 and 5 ppm for 4-hexen-3-one, 5-hexen-2-one and 3-penten-2-one respectively. The degradation of unsaturated ketones would lead to significant amount of ozone formation in the troposphere. This is added in the RMS.