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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.

Ms. Title: Experimental and computational kinetics investigations for the reactions of Cl atoms with unsaturated ketones in gas phase

In the present work, the authors report experimentally and theoretically obtained rate coefficients for the reaction of Cl atoms with three unsaturated ketones, i. e., $CH_3CH=CHC(O)C_2H_5$, $CH_2=CH(CH_2)_2C(O)CH_3$ and $CH_3CH=CHC(O)CH_3$ that are abundant in the atmosphere, employing relative rate methods and ab-initio calculations ($CCSD(T)/6-31+G(d,p)//MP2/6-311++G(d,p)$), respectively. In addition to that, the temperature dependence of the title reactions was also studied, both experimentally (298 – 363 K) and theoretically (275 – 400 K), at atmospheric pressure. Finally, ab initio calculations were also used to facilitate reaction mechanism investigation.

The present reviewer believes that the present study does fit in ACP, but there are several, both major and minor issues that the authors need to address before the current submission would be in a publishable form.

Minor issues:

R3Q1. All the sentences that start with *witch* and *where* should include a comma before that, i.e., *,which*, throughout the manuscript.
Response: We have included "comma" before which and where throughout the manuscript.

R3Q2. Keywords should be one word

Response: We have written as "Keyword" in the RMS. All the keywords were written in one word format.

R3Q3. Pg 2. line 9, Introduction: Please change *effects* with *affects*.
Response: Corrected.

R3Q4. Pg 2. line 12, Introduction: Please rephrase *abundant attention*
Response: We have replaced "abundant attention" with "lot of attention".

R3Q5. **Pg 3. line 1, Introduction:** Please change *different* with *the dominant*
Response: We have replaced "different" with "dominant".

R3Q6. **Pg 3. line 6, Introduction:** Please change *reported them to be* to *the reported values were*
Response: Corrected.

R3Q7. **Pg 3. line 16 Introduction:** Please note that data is a count noun when you refer to experimental data and through the whole text you should change the syntax of *data is* with *data are*.
Response: corrected throughout the RMS.

R3Q8. **Pg 5. line 22 Chemicals:** Please replace *freeze-pump-thaw* with *freeze-pump-thaw cycle*
Response: "freeze-pump-thaw" is replaced with "freeze-pump-thaw cycle" in the RMS.

R3Q9. In the reaction scheme the temperature range given is wrong (200 – 400 K). Please correct accordingly.
Response: corrected to appropriate temperatures: 298 – 363K, Experiment & 275-400K, Theory.

R3Q10. There are several similar issues that the authors should address in the whole paper. It is strongly recommended fresh eyes should read through the whole text.

Response: We have gone through the whole manuscript and all grammatical mistakes and misspellings were corrected.

Major issues:

Title:

R3Q11. Among the three test compounds studied in the present work, only two were looked into experimentally, which probably mean that the word series should be omitted from the paper title.

Response: It was removed in the RMS. After removing it, the new title is "Experimental and computational kinetics investigations for the reactions of Cl atoms with unsaturated ketones in gas phase".

R3Q12. Include the pressure conditions and the bath gas (Include those conditions in tables as well) used in the majority of the experiments in Abstract section.

Response: The pressure conditions and bath gas used are given both in the abstract and the Tables 1 and 2. These two tables are appended below for the reviewer's ready reference.

Table 1: Relative rate measurements for the reaction of Cl atoms with 4-hexen-3-one over the temperature range of 298-363K relative to 1,3-butadiene, isoprene and 1-pentene.

T(K)	Reference compound	Bath gas (Torr of O_2)	Pressure in Torr	$(k_{sample}/k_{reference}) \pm 2\sigma$	$(k_{sample}/k_{reference})$ Average$\pm 2\sigma$	$(k\pm 2\sigma)\times 10^{-10}$ cm^{3}molecule^{-1}s^{-1}	$(k\pm 2\sigma)\times 10^{-10}$ cm^{3}molecule^{-1}s^{-1}	Literature $(k\pm 2\sigma)\times 10^{-10}$ (cm^{3}molecule^{-1}s^{-1}) at 298K
298±2	1,3-butadiene	N_2	760	1.55±0.21 1.43±0.24 1.64±0.27	1.54±0.27	5.10±0.81		
	isoprene	N_2	760	1.63±0.15 1.62±0.11 1.60±0.13	1.61±0.14	5.84±0.80	5.55±1.31	3.00±0.58 Blanco et al.
	1-pentene	N_2	760	1.12±0.12 1.09±0.13 1.33±0.10 1.33±0.10	1.21±0.19	5.71±0.62		
	isoprene	$N_2 - O_2$ (20)	760	1.57±0.14 1.61±0.11	1.59±0.11	5.74±0.18	5.74±0.18	
	isoprene	N_2	600	1.58±0.09	1.55±0.10	5.61±0.25	5.61±0.25	

				1.53±0.13			
	isoprene	N_2	500	1.59±0.11	1.57±0.10	5.67±0.18	5.67±0.18
				1.55±0.12			
310±2	1,3-butadiene	N_2	760	1.49±0.12	1.50±0.13	4.67±0.06	
				1.51±0.16			
	isoprene	N_2	760	1.24±0.10	1.29±0.13	4.13±0.22	4.20±0.47
				1.37±0.10			
				1.26±0.09			
	1-pentene	N_2	760	0.93±0.01	0.89±0.07	3.82±0.38	
				0.86±0.06			
330±2	1,3-butadiene	N_2	760	1.35±0.14	1.33±0.13	4.06±0.15	
				1.31±0.11			
	isoprene	N_2	760	1.24±0.10	1.15±0.13	3.36±0.20	3.45±0.25
				1.13±0.09			
				1.09±0.08			
	1-pentene	N_2	760	0.79±0.04	0.80±0.07	2.95±0.07	
				0.81±0.04			
350±2	1,3-butadiene	N_2	760	1.29±0.15	1.30±0.14	3.43±0.10	
				1.32±0.12			
	isoprene	N_2	760	0.98±0.07	1.06±0.13	2.84±0.26	2. 89±0.28
				1.19±0.10			
				1.01±0.08			
	1-pentene	N_2	760	0.74±0.05	0.74±0.10	2.42±0.03	
				0.75±0.06			
363±2	1,3-butadiene	N_2	760	1.24±0.09	1.26±0.11	3.31±0.13	
				1.28±0.12			
	isoprene	N_2	760	0.87±0.4	0.86±0.08	3.01±0.10	2.60±0.19
				0.88±0.2			
				0.85±0.6			
	1-pentene	N_2	760	0.74±0.02	0.72±0.11	2.18±0.09	
				0.72±0.06			
				0.71±0.05			
	1,3-butadiene	$N_2 - O_2$ (20)	760	1.30±0.11	1.28±0.11	3.38±0.10	3.38±0.10
				1.27±0.09			

Table 2: Relative rate measurements for the reaction of Cl atoms with 5-hexen-2-one over the temperature range of 298-363K relative to 1,3-butadiene, isoprene and 1-pentene.

T (K)	Reference compound	Bath gas (Torr of O_2)	Pressure in Torr	$(k_{sample}/k_{reference}) \pm 2\sigma$	$(k_{sample}/k_{reference})_{Average} \pm 2\sigma$	$(k \pm 2\sigma) \times 10^{-10}$ $(cm^3 molecule^{-1}s^{-1})$	$(k_{Average} \pm 2\sigma) \times 10^{-10}$ $(cm^3 molecule^{-1}s^{-1})$	Lite.$k \times 10^{-10}$ $(cm^3 molecule^{-1}s^{-1})$ at 298K
298±2	1,3-butadiene	N_2	760	1.24±0.13 1.26±0.10 1.29±0.11	1.26±0.15	4.19±0.63	4.14±1.25	3.15±0.5 Blanco et al.
	isoprene	N_2	760	1.18±0.09 1.14±0.10 0.97±0.16	1.09±0.20	3.95±0.97		
	1-pentene	N_2	760	0.87±0.09 0.95±0.08 0.91±0.08	0.91±0.16	4.27±0.38		
	isoprene	$N_2 - O_2$ (20)	760	1.13 ±0.11 1.11±0.09	1.12±0.12	4.03±0.56	4.03±0.56	
	isoprene	N_2	600	1.15±0.12 1.19±0.10	1.17±0.13	4.21±0.61	4.21±0.61	
	isoprene	N_2	500	1.16±0.14 1.15±0.11	1.15±0.15	4.16±0.58	4.16±0.58	
310±2	1,3-butadiene	N_2	760	1.14±0.12 1.12±0.10	1.13±0.13	3.51±0.06	3.68±0.30	
	isoprene	N_2	760	1.06±0.08 1.13±0.06	1.09±0.09	3.50±0.28		
	1-pentene	N_2	760	0.94±0.08 0.95±0.09	0.94±0.12	4.04±0.04		
330±2	1,3-butadiene	N_2	760	1.11±0.13 1.10±0.12	1.10±0.16	3.37±0.03	3.20±0.15	
	isoprene	N_2	760	1.05±0.06 1.09±0.08	1.07±0.09	3.11±0.14		
	1-pentene	N_2	760	0.84±0.06 0.85±0.04	0.84±0.08	3.12±0.03		
350±2	1,3-butadiene	N_2	760	1.02±0.14 1.06±0.09	1.04±0.16	2.73±0.13	2.91±0.25	
	isoprene	N_2	760	1.17±0.16 1.12±0.13	1.14±0.17	3.07±0.18		
	1-pentene	N_2	760	0.92±0.10 0.89±0.09	0.90±0.14	2.94±0.13		
363±2	1,3-butadiene	N_2	760	1.05±0.12 1.09±0.09 1.12±0.11	1.08±0.17	2.86±0.18	2.70±0.31	
	isoprene	N_2	760	0.98±0.07	1.02±0.13	2.60±0.25		

			0.99±0.09				
			1.10±0.08				
1-pentene	N_2	760	0.89±0.05	0.88±0.08	2.65±0.03		
			0.87±0.06				
1,3-butadiene	$N_2 - O_2$ (20)	760	1.11±0.09	1.09±0.10	2.88±0.10	2.88±0.10	
			1.08±0.07				

R3Q13. Authors report uncertainties in the abstract and in all other sections of the paper, tables etc., but there is no explanation of how were they determined and what they represent. Do they include systematic uncertainties and if they do, how were they estimated? An error analysis section will assist the reader to go through the paper and assess the reliability of the measurements.

Response: We have re calculated errors and a separate section was included on error analysis in the RMS as mentioned below.

"The uncertainties in the temperature (within ±2K) and pressure (within ±1 Torr) in the reaction chamber were very small and did not contribute significantly on the determination of the rate coefficients. The elution of the test molecules and reference compounds in the GC are precise and the uncertainty in concentrations was estimated to be less than 5%. For each experiment, the obtained slopes (using linear least squares method) along with the errors (95% confidence limit) are given in Tables 1 and 2. The uncertainties on the weighted average slopes $((k_{sample}/k_{reference})_{Average})$ are determined using the error propagation method according to the equation: $\Delta y/y = [[\Delta a/a]^2 + [\Delta b/b]^2 + \dots]^{1/2}$, where $\Delta y/y$ is the relative error on the average slope and $[\Delta a/a]$, $[\Delta b/b]$ are the relative errors on the individual slopes. The errors quoted for the rate coefficients also include the quoted error in the rate coefficients for the reference reactions and are calculated using the standard error propagation method which was used by several groups (Blanco et al., 2009; Stoeffler et al., 2013; Peirone et al., 2014 and Dash et al., 2015) according to the equation: $\Delta k_{test} = k_{test} \times [(\Delta k_{ref}/k_{ref})^2 + (\Delta(k_{test}/k_{ref})/ (k_{test}/k_{ref}))^2]^{1/2}$, where $(\Delta k_{ref}/k_{ref})$ and $\Delta(k_{test}/k_{ref})/(k_{test}/k_{ref})$ are the relative errors on k_{ref} and k_{test}/k_{ref}, respectively. At every temperature, the uncertainties in the averaged rate coefficients were calculated according to the equation: $\Delta k_{average} = k_{average} \times [[\Delta l/k_l]^2 + [\Delta m/k_m]^2 + [\Delta n/k_n]^2]^{1/2}$, where Δl, Δm and Δn, are the relative errors on the individual rate coefficients and k_l, k_m and k_n are individual rate coefficients.

A major source of systematic errors in the determination of the title reaction's rate coefficients are from the absolute uncertainties in the rate coefficients of the reference reactions.

Blanco, M. B., Bejan, I., Barnes, I., Wiesen, P., Teruel, M. A. Temperature-dependent rate coefficients for the reactions of Cl atoms with methyl methacrylate, methyl acrylate and butyl methacrylate at atmospheric pressure. Atmos. Environ. 43, 5996–6002, 2009.

Stoeffler, C., Joly, L., Durry, G., Cousin, J., Dumelie, N., Bruyant, A., Roth, E., Chakir, A. Kinetic study of the reaction of chlorine atoms with hydroxyacetone in gas-phase. Chem. Phys. Lett. 590, 221–226, 2013.

Peirone, S. A., Barrera, J. A., Taccone, R. A., Cometto, P. M., Lane, S. I. Relative rate coefficient measurements of OH radical reactions with (Z)-2-hexen-1-ol and (E)-3-hexen-1-ol under simulated atmospheric conditions. Atmos. Environ. 85, 92-98, 2014.

Dash, M. R., Srinivasulu, G., Rajakumar, B. Experimental and computational investigation on the gas phase reaction of p-cymene with Cl atoms. J. Phys. Chem. A 119, 559−570, 2015.

R3Q14. In general, the present reviewer believes that the submitted draft needs severe reorganization as theoretical calculations and experimental results for each ketone have substantial similarities. It would be more meaningful to present experimental results for both ketones and they should be separate from the corresponding theoretical ones, to avoid repetitions. Then, the authors might include a section where all the important observations would be summarized and comparisons between experiments and theory, relative positioning of the double bond and carbonyl group (experiment vs experiment and theory vs theory) should be highlighted and interpreted in terms of reactivity.
Response: We have reorganized the paper and all experimental and all theoretical results in separate sections for better comparison between similar molecules.

R3Q15. Although $CH_3CH=CHC(O)CH_3$ vapour pressure is low, it should be adequate for relative rate measurements, especially at higher temperatures. Experiments, even at those conditions would assist to understand how the relative positioning of the double bond and carbonyl group affects unsaturated ketones reactivity, as well as what the impact to the compete

reaction mechanisms of abstraction and association is. It might also be of worth to try to do some experiments with the title ketone, especially at high temperatures.

Response: In the present manuscript, the experiments were performed on 4-hexen-3-one and 5-hexen-2-one only. Just to understand the mechanism for the reactions of Cl atom reactions with unsaturated ketones, 3-penten-2-one was also studied using computational methods along with 4-hexen-3-one and 5-hexen-2-one.

R3Q16. Regarding theoretical calculations: a. How the authors verified that they have located global minima on the PES, during geometries optimization. b. Although the authors employed a level of theory of high accuracy (CCSD(T)), the basis set used was unexpectedly limited. Why did the authors chose a non-correlation consistent, double zeta basis set for single point calculations? c. Although it is reasonable, the authors should clearly state that they have also calculated ZPE using MP2 method and that they have calculated their values at 296 K.

Response: We have optimized all the possible conformers during geometry optimization. The lowest energy conformers were considered for rate coefficients calculations. Whereas other possible conformers are more than 1.9 kcal mol^{-1} higher in energy than the lowest energy conformers and therefore, it is unlikely to have significant contribution to the reaction in the temperature range of our study.

We employed 6-311++G(d,p), cc-pvdz and aug-cc-pvdz basis sets for single point energy calculations of the title reactions. The obtained rate coefficients with these basis sets were over estimated when compared with the present experimental and reported rate coefficients for the title reactions. Therefore, 6-31+G(d,p) basis set was used for single point calculations and ZPE energies obtained at MP2 level of theory were also included in our calculations.

R3Q17. Reference reactions were measured in a narrower temperature range compared to the studied reactions. This is to say that the authors have assumed that reaction mechanism does not change as a function of temperature. This might be partly true and safe when reactions proceed only via –H abstraction, which is not the case here, where abstraction and association compete to each other and their contribution is expected to vary with temperature. It is strongly recommended the authors to avoid such assumptions and hypothetical extrapolations. It would have also been more appropriate to use as references, reactions that the rate coefficient is not

pressure dependent. On the top of that, the authors recognize that pressure dependent measurements would assist to understand the mechanism of the reaction and they will reveal how the competition between the pressure independent channels of H abstraction competes with the pressure dependent pathway of Cl association to the double bond. From an atmospheric perspective, those very short lived compounds (VSLC) will not be substantially transferred to the upper troposphere ad thus rate coefficient measurements at atmospheric pressure are the most relevant ones with regard to the atmospheric impact.

Response: Several groups have measured the rate coefficients of Cl atom reactions with many unsaturated hydrocarbons at room temperature (298K). However, temperature dependent rate coefficients are available only for 1-pentene (Coquet et al., 2000) and isoprene (Bedjanian et al., 1998) in the temperature range of 233-320K. Also, the rate coefficients of these reactions are close to the rate coefficients of the title reactions, which is a pre requisite to use them as reference compounds in the relative rate method. Therefore, 1-pentene and isoprene were used as reference compounds in the present investigation. As reviewer rightly pointed out, our present studies were carried out in the temperature range of 298-363K whereas, the reference reaction's rate coefficients are available in the temperature range of 233-320K only. Therefore, technically the measured rate coefficients in the higher temperature range (321-363K) may not be reliable. Recently, we have measured the temperature dependent rate coefficients in the temperature range of 269-363K for the reaction of Cl atoms with 1,3-butadiene (Vijayakumar et al., 2017). Now, we have measured the temperature dependent rate coefficients (in the temperature range of 298-363K) for the title reactions using 1,3-butadiene + Cl reaction as a third reference reaction . The measured rate coefficients are given in Tables 1 and 2. From these tables, it is clear that the rate coefficients obtained using all the three reference compounds (1,3-butadiene, isoprene and 1-pentene) are very close to each other over the studied temperature range within the experimental uncertainties. Therefore, the obtained rate coefficients relative to 1,3-butadiene, isoprene and 1-pentene were averaged at the respective temperatures. With this additional input, the rate coefficient data obtained is reliable in the entire studied range of temperature.

Vijayakumar, S., Rajakumar, B. Experimental and theoretical investigations on the reaction of 1,3-butadiene with Cl atom in the gas phase. J. Phys. Chem. A 121, 1976-1984, 2017.

R3Q18. Mechanism was not thoroughly investigated and no critical SOA formation intermediates were identified. The part that the authors try to interpret the mechanism in terms of electronic effects due to the presence of carbonyl group is incomplete and steric factors and entropy change to the TS should be also considered. A comparative plot of the abstraction and association kinetics as a function of temperature would assist to elucidate the relative importance.

Response: As we have discussed in section 3.7, the atmospheric degradation mechanism was proposed till the chloroalkyl radicals are formed. It was proposed based on our theoretical observations. The contribution of abstraction channels as a function of temperature is given in Figures 12 to 14 (branching ratios plots) and the same discussed in the text (*c.f.* section 3.4). In fact the branching ratios clearly reveal that the association reactions are dominant. The variation of the rate coefficients with respect to temperature both in case of abstraction and association is shown in the branching ratio plots.

Tables:

R3Q19. Relative rate tables: In all cases ratios uncertainties and bimolecular rate coefficients ones are identical, which is to say that the authors have not propagated the error limits.

Revision is required through the whole draft. (e.g., Table 1. r = 1.46 ±**0.36** and k =(5.08±**0.36**) ×10-10 cm3 molecule-1 s-1). The sources of the quoted uncertainties should also be included.

Response: Complete error analyses was carried out again and now we have reported the corrected errors. For details, please refer to our response to R3Q13 of this reviewer.

R3Q20. **Table 4.** The authors report a rate coefficient of 1.09 ×10-9 cm3 molecule-1 s-1 at 275K that is higher than the collision rate limit (~8 ×10-10 cm3 molecule-1 s-1 at room temperature). This is possible only when reaction follows a Harpoon mechanism, which means ion-ion or ion-molecule interaction, which definitely is not the case here. Most likely, this is due to intrinsic problems of the computational methods and if there was an estimated uncertainty of the calculated k values via benchmarking calculations, the error limits would have revealed that this is due to the limitations of the theoretical methods employed.

Response: In case of Cl atom reaction with 5-hexen-2-one (*c.f.* Table 4), the rate coefficients for the reaction below 275 K are touching the gas kinetic limit. This kind of behavior is expected in case of the ion-ion or ion-molecule interaction or radical – radical reactions. May be this is due

to the presence of Cl atom/radical in the title reaction. The reaction is totally governed by the addition of Cl atom at the double bond present in the substrate. Addition channels are exothermic. Also, these channels are feasible both kinetically (because of the submerged transition states) and thermodynamically. As the reaction is dominant and proceed via negative transition states, the rate of reaction increases with the decrease in temperature. All these would probably favor the reaction at low temperatures to the largest possible extent. In addition, as the reviewer rightly pointed, there may be intrinsic limitations of the theory chosen for these calculations as well. This is added in the RMS.

Graphs:

R3Q21. All the relative rate plots should begin from zero difference in test and reference concentration relative variance (0,0). Negative values are meaningless. Moreover, figure captions should include all the experimental conditions and explain everything that is shown inside the plots and in insets of the graph. Finally, for the shake of clarity, please use different symbols when different references are included in the graph (Not only different colors).

Response: It was corrected in the RMS as shown below.
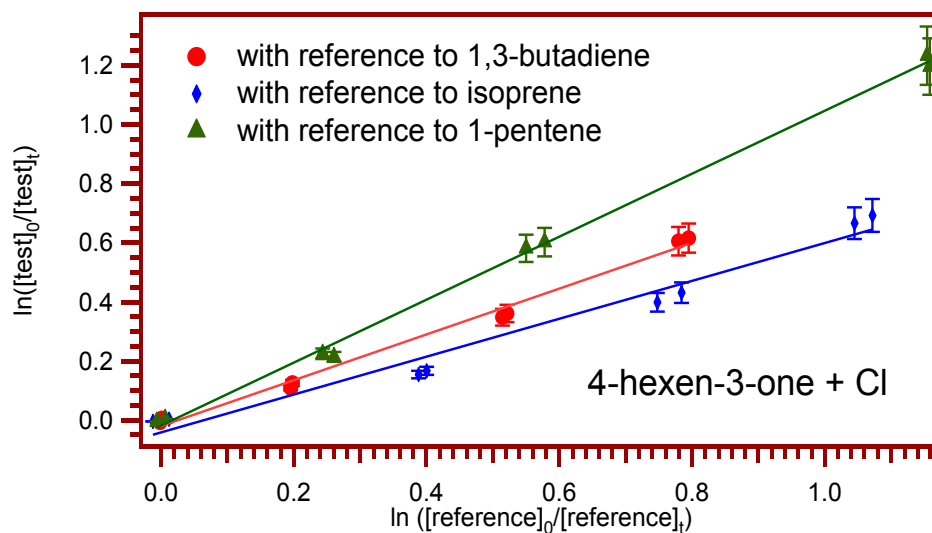

Figure 1: Plot of the relative decrease in the concentration of 4-hexen-3-one due to its reaction with Cl atoms relative to 1,3-butadiene, isoprene and 1-pentene at 298K and 760 Torr of N_2. The symbols indicate measurements made relative to different compounds as indicated in the legend. These lines are linear least squares fits of the data to equation 1 that yield rate coefficients for reaction 1. The error bars are from the precision of the measurement.
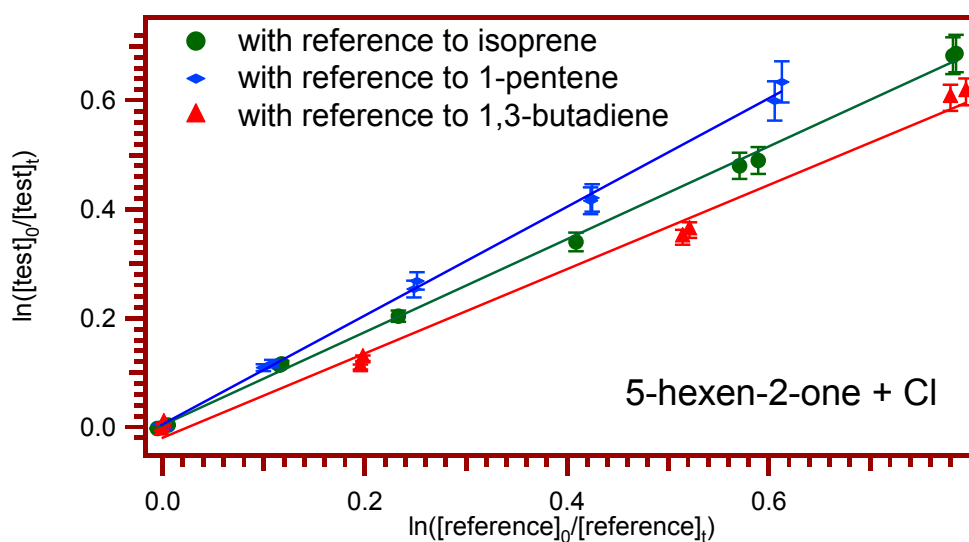
Figure 3: Plot of the relative decrease in the concentration of 5-hexen-2-one due to its reaction with Cl atoms relative to 1,3-butadiene, isoprene and 1-pentene at 298K and 760 Torr of N_2. The symbols indicate measurements made relative to different compounds as indicated in the legend. These lines are linear least squares fits of the data to equation 1 that yield rate coefficients for reaction 2. The error bars are from the precision of the measurement.

R3Q22. In Arrhenius plots, first, include an X-mirror axis so as the reader to have a measure of temperature. Also, use k (and log axis) in Y-axis. Note that lnk has no units and if the authors decide to keep it this way, they should refer to it as ln (k, cm3 molecule-1 s-1).

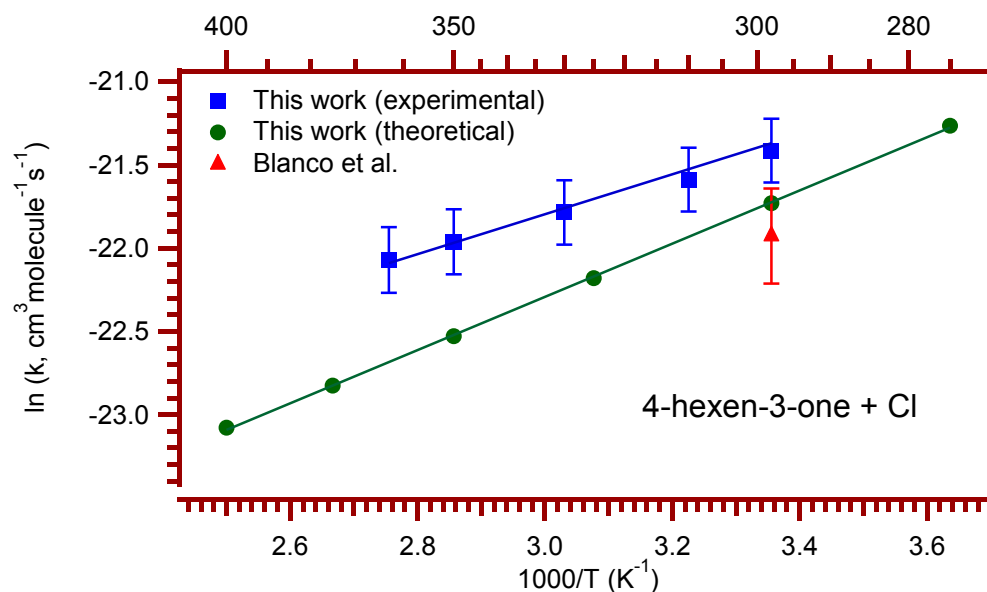**Response:** It was corrected in the RMS as shown below.

Figure 2: Arrhenius plot of CVT/SCT rate coefficients calculated at the CCSD(T)/6-31+G(d, p)//MP2/6-311++G(d,p) level of theory between the temperatures 275 and 400 K and experimentally measured rate coefficients between the temperatures of 298 and 363 K for the reaction of Cl atoms with 4-hexen-3-one.
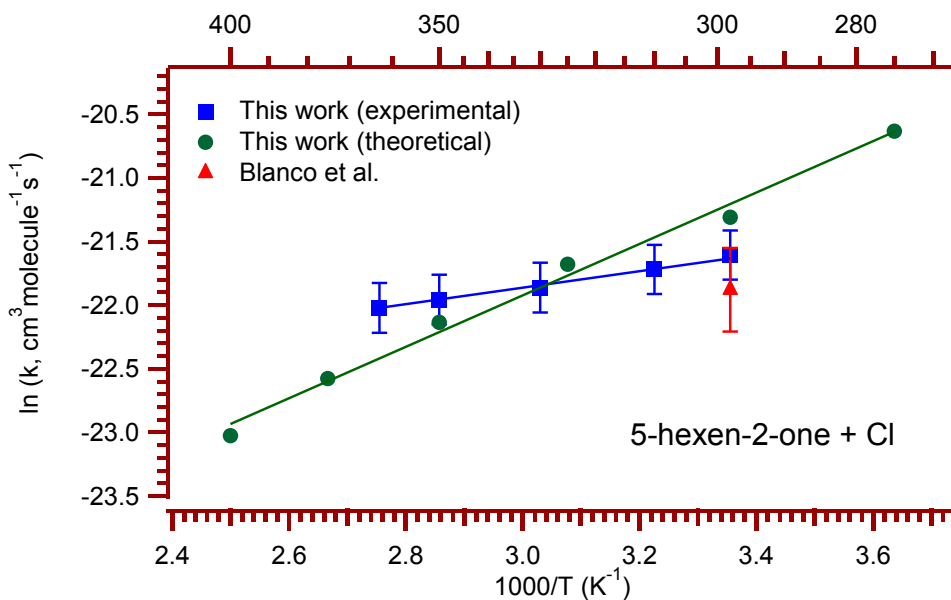

Figure 4: Arrhenius plot of CVT/SCT rate coefficients obtained at the CCSD(T)/6-31+G(d, p)//MP2/6-311++G(d,p) level of theory between the temperatures 275 and 400 K and experimentally measured rate coefficients between the temperatures of 298 and 363 K for the reaction of Cl atoms with 5-hexen-2-one.
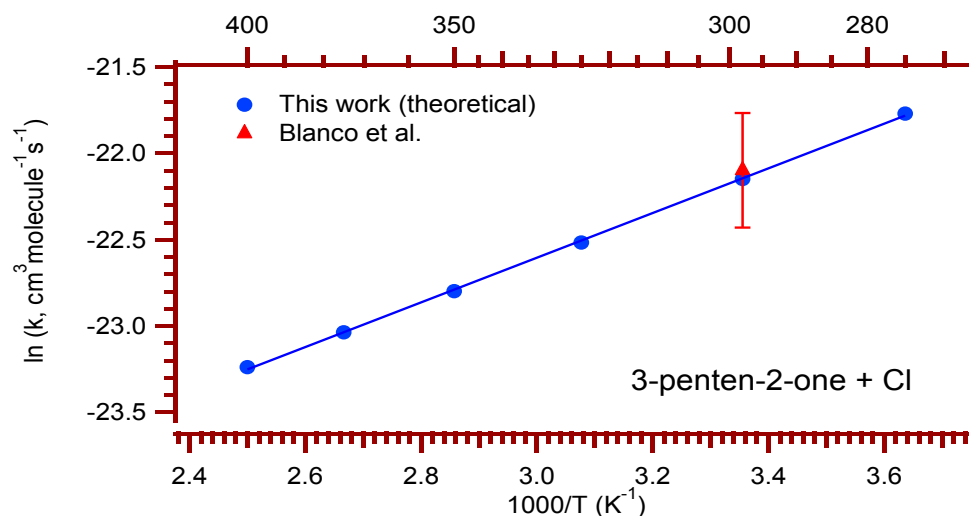
Figure 11: Arrhenius plot of CVT/SCT rate coefficients obtained at the CCSD(T)/6-31+G(d, p)// MP2/6-311++G(d,p) level of theory between the temperatures 275 and 400 K for the reaction of Cl atoms with 3-penten-2-one.

R3Q23. In some cases, curvature was observed in Arrhenius plot. Why didn't the authors fit their data using a modified version of Arrhenius fitting (A ×Tn), which include temperature dependence on the pre-exponential factor and is quite common in association reactions.

Response: In Figure 2, after adding third reference compound, it is showing a liner behavior and used linear least square method to fit the experimental data and shown below.
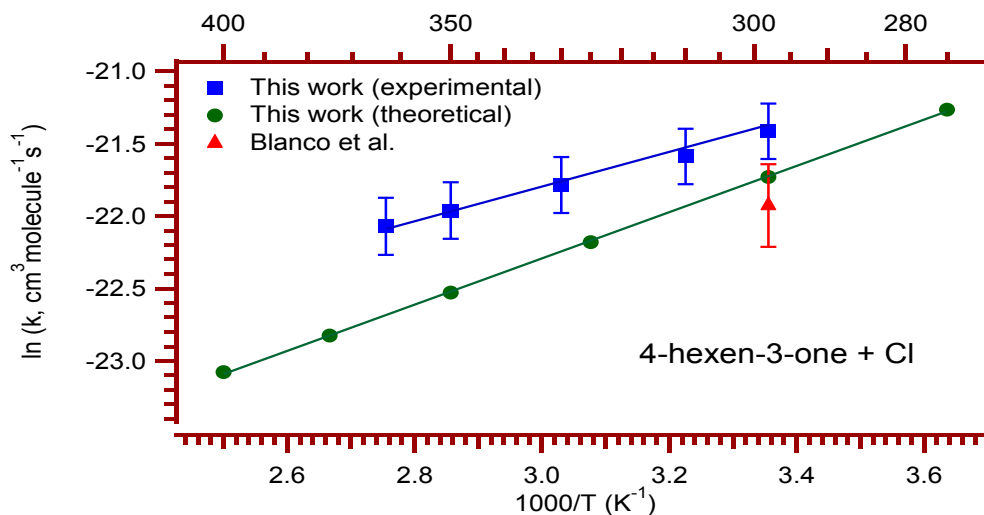

Figure 2: Arrhenius plot of CVT/SCT rate coefficients calculated at the CCSD(T)/6-31+G(d, p)//MP2/6-311++G(d,p) level of theory between the temperatures 275 and 400 K and experimentally measured rate coefficients between the temperatures of 298 and 363 K for the reaction of Cl atoms with 4-hexen-3-one.

Conclusions:

R3Q24. Conclusions are very limited and not appropriate for such an amount of work.

Response: We have included some more points in the RMS as mentioned below.

"In this study, reactions of Cl atoms with 4-hexen-3-one (R1), 5-hexen-2-one (R2) and 3-penten-2-one (R3) were investigated. R1 and R2 were investigated experimentally in the temperature range of 298-363K; whereas R1, R2 and R3 were studied computationally. The rate coefficients for all the reactions were calculated by CVT/SCT coupled with CCSD(T)/6-31+G(d,p)//MP2/6-311++G(d,p) level of theory. Addition of Cl atom across the double bond in all the reactions predominates and abstraction of hydrogen would have very insignificant contribution to the overall reaction. From both experimental and theoretical measurements, negative temperature dependence was observed over the studied temperature range because of the submerged transition states for addition channels. Thermodynamically, the addition reactions are more feasible and spontaneous. The reactions of Cl atoms with test molecules are much faster than the other dominant reactions (OH radicals, O_3 molecules and NO_3 radicals) especially in polluted mid –continental regions, in industrial locations, in marine boundary layers and in urban polluted areas where the Cl atom concentrations reaches maximum up to 10^5 atoms cm^{-3}. The cumulative lifetimes of the test molecules are very low and they are lost within few hours as soon as they are released into the atmosphere. The Cl atom initiated reactions with unsaturated ketones leads to the formation of halogenated ketones and a variety of organic nitrates, in the nitrogen rich environment. On further reactions with NO_x, these compounds form thermally stable secondary organic nitrates which may show significant impact on the air quality and climate change of the Earth's atmosphere. However, the atmospheric lifetimes of unsaturated ketones are relatively short which suggest their inconsiderable impact on the global warming. The degradation of unsaturated ketones would lead to significant amount of ozone formation in the troposphere". This is added in the RMS.

R3Q25. GWP contribution is negligible, since the studied ketones contain no C-F bonds and more importantly they are very short lived compounds. Did the authors look if there are any available IR spectra in the literature that they can comment on them to justify their statements?

Response: We have calculated GWPs for test molecules and estimated them to be 0.01, 0.01 and 0.01 for 4-hexen-3-one, 5-hexen-2-one and 3-penten-2-one respectively for 20 years time

horizon. Hence, we have stated that GWPs for test molecules seems to be negligible. We have searched for the IR spectra in the literature and are not reported till date to the best of our knowledge. Therefore, we are not in a position to compare our data.

R3Q26. The authors could estimate a POCP (photochemical ozone creation potentials) for the studied ketones and compare with similar unsaturated compounds. This is expected to be the major contribution of those compounds on air-quality issues.

Response: We have calculated ozone formation potentials in the troposphere for the title reactions and found to be 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.

R3Q27. Cl chemistry importance should be commented in conclusion part. Although it is not expected to substantially affect the fate of ketones, since they are extremely short lived compounds, it might be of importance if chlorinated products are formed. In particular for such short lived compounds it might also affect their POCP, taking into account that metropolitan cities and polluted areas are responsible for the huge majority of emissions of such compounds and in most of the cases they are located near by the sea, where the higher levels of Cl atoms are observed.

Response: The importance of the Cl atom chemistry is discussed for the query 1 (R3Q24) of the conclusion part. This is added in the RMS.