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Ms. Title: Experimental and computational kinetics investigations for the reactions of Cl atoms with series of 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., $CH_3CH=CHC(O)C_2H_5$, $CH_2=CH(CH2)_2C(O)CH_3$ 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 calculation 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:

1. All the sentences that start with *witch* and *where* should include a comma before that, i.e., *,which*, throughout the manuscript.
2. Keywords should be one word
3. **Pg 2. line 9, Introduction:** Please change *effects* with *affects*.
4. **Pg 2. line 12, Introduction:** Please rephrase *abundant attention*
5. **Pg 3. line 1, Introduction:** Please change *different* with *the dominant*
6. **Pg 3. line 6, Introduction:** Please change *reported them to be* to *the reported values were*
7. **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*.
8. **Pg 5. line 22 Chemicals:** Please replace *freeze-pump-thaw* with *freeze-pump-thaw cycle*

9. In the reaction scheme the temperature range given is wrong (200 – 400 K). Please correct accordingly.

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.

Major issues:

Title:

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.

1. 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.

2. 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.

3. In general, the present reviewer believes that the submitted draft needs severe reorganisation 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.

4. 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.

5. Regarding theoretical calculations: a. How the authors verified that they have located global minima on the PES, during geometries optimisation. 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.

6. 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.

7. 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.

Tables:

1. 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) $\times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}). The sources of the quoted uncertainties should also be included.

2. **Table 6.** The authors report a rate coefficient of 1.09×10^{-9} cm^3 $molecule^{-1}$ s^{-1} at 275 K that is higher than the collision rate limit (~8×10^{-10} cm^3 $molecule^{-1}$ 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.

Graphs:

1. 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).
2. 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, cm^3 $molecule^{-1}$ s^{-1})
3. In some cases, curvature was observed in Arrhenius plot. Why didn't the authors fit their data using a modified version of Arrhenius fitting ($A \times T^n$), which include temperature dependence on the pre-exponential factor and is quite common in association reactions.

Conclusions:

1. Conclusions are very limited and not appropriate for such an amount of work.
2. 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?

3. The authors could estimate a POCP 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.

4. 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 af Cl atoms are observed.