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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #1

Received and published: 8 May 2017

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-

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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. Maybe Hindered rotor treatment can solve the discrepancy of the computational rate with the reference rate (experimental). I can see in Figure 2, the rate coefficient agree within 50% with the reference value and previously measured value. However, the calculated rate coefficient at the lower temperature ($\sim$275K) is near about a factor of 10 and at the higher temperature (400K) it is $\sim$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 maybe gives you closer value in the entire temperature range. You can find the error in the energy calculation based previous papers JPC A 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.

Minor Comments:

Abstract No need to write a full description of Arrhenius expressions. Maybe something like k1 = ——, k2 =. . ..will work.

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. Line 17-19: these ketones, please be specific. Page 5 line 11: Why rate expression is in the bold letter? Need equation number.

Computational Methodology Page 1 Line 1: MP2 calculations are based on full electrons or based on frozen cores? Page 1 line 3: What are the reactive complexes (RCs)? I think it should be PRC (Pre-reactive Complex). Page 1 line 5: IRC calculation at MP2 level for what reason?

Results and Discussion Page 7 Line 3: “Maybe 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.

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

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

Figure 4. PES is incomplete; I don’t see the PRC energy. I guess the Electronic + ZPE is calculated at 0 K. Not sure that if authors have included thermal corrections?

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

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.

Figure 8 and 9: Structure of RC2a is missing. If RC1a and RC2a are structurally and energetically same, then why two different pre-reactive complexes?

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

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

Table 9: Something wrong with title or table contents.

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.

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