

GENERAL COMMENTS

This manuscript reports relative rate experiments and computations on the kinetics of Cl reacting with a series of unsaturated ketones as a function of temperature. These compounds are of some interest and the reaction of Cl with these compounds can contribute significantly to their loss under some atmospheric conditions. The experiments (on two compounds) appear to be solid, although additional details should be reported and the clarity improved. Also, there is no experimental rate constant data on the reference compounds at the higher temperatures studied here. As a result, the absolute rate constants (as opposed the relative rate constants) at those higher temperatures may not be reliable.

The clarity and precision of the writing should be improved.

The computational chemistry calculations are not reliable. While it the authors could address issues with the energetics obtained from quantum chemistry, it is probably not feasible to reliably compute rate constants and branching ratios for the systems being studied here.

I am uncertain as to the importance of the two compounds being studied experimentally, and the experiments only provide rate constants, not branching ratios. So the manuscript remaining after removing the computational parts probably does not belong in ACP.

SPECIFIC COMMENTS ON EXPERIMENTS

1. Secondary chemistry appears to be a minor factor, but the reference compounds are sufficiently similar that they might give rise to similar secondary chemistry. It would help to present a brief discussion about WHY secondary chemistry is expected be minor. Just in case someone wants to model the experiment, the manuscript should include the repetition rate of the 248 nm lasers and its fluence (in $\text{mJ cm}^{-2} \text{ pulse}^{-1}$ rather than mJ pulse^{-1}). For the same reason, the initial concentration range of the test compounds and reference compounds should be listed in the text.

2. An expanded version of Table 1 is needed that includes the initial concentration of the reference compound. Also, results should be presented with experiments with O_2 present.

Ideally, the Supplementary Material would include the measured concentration of the test compounds and the reference compound at 1200, 1400, 1600, 1800 and 2000 pulses for each experiment.

3. The literature values of the rate constant for Cl + isoprene and Cl + 1-pentene are only known up to 320 K. There is no reason to expect Arrhenius behavior from these reactions. Consequently, it is not appropriate to derive absolute rate constants at these temperatures without highlighting the fact that rate constants for the reference compounds are being extrapolated.

4. The value of [Cl] used to compute atmospheric lifetimes (in Table 10) is only valid in a small part of the atmosphere. This should be noted.

SPECIFIC COMMENTS ON CALCULATIONS

1. The CCSD(T) energy calculations use a basis set that is far too small to be reliable. This is evident in many of the reported values of the critical energies for hydrogen abstraction (they are far too high). Could there also be a problem with unstable wavefunctions contributing to high energies of these TSs? The small basis set could also (via basis set superposition error) lead to TS energies for the addition reaction that are lower than the actual values. The fact that the reported rate constants (dominated by addition) agree with experiment is due to fortuitous cancellation of error. A basis set extrapolation scheme or composite method is needed for accurate treatment of both types of TSs.

2. The addition of Cl to the test compounds to form a reactive complex must have a variational TS (in addition to the saddle point reported for the formation of a covalent chlorine-carbon bond). Strictly speaking, a 2-TS approach is needed to obtain the rate constant in the high-pressure limit (see J. Phys. Chem. A, 2006, 110, pp 6960–6970), but I would not insist on authors carrying out these calculations.

The manuscript implicitly assumes the addition reactions are in the high pressure limit at 1 atm over the temperature range reported. This may be reasonable, but should be stated explicitly.

3. There is an issue with the computations that the authors won't be able to overcome: the general approach used here probably has limited applicability to Cl reaction with molecules containing C=C double bonds. See the 2014 paper by A.G. Suits and A. M. Mebel (DOI: 10.1038/ncomms5064). This paper makes two major points relevant here:

a) H-abstraction from allylic sites proceeds without a barrier (3-penten-2-one and 4-hexen-3-one have allylic sites).

b) There exists roaming paths connecting chlorine adducts of the alkenes to HCl formation (potentially relevant to all three species studied in the manuscript under review).

The results in this paper have been verified and extended. The reaction paths described in (a) and (b) are important under the conditions of the experiment, and (a) is important. Although those conditions are far different than those in the atmosphere, another paper (DOI: 10.1038/srep40105) suggests that roaming paths leading to HCl are more important at thermal energies (meaning atmospheric conditions) than the conditions of the Suits and Mebel paper. This conclusion

The results found in this manuscript are not consistent with those of the Suits and Mebel paper or subsequent computations. The roaming paths can only be treated by running dynamics, and that is far outside the scope of this manuscript. As a result, it appears that reliable kinetic insight cannot be obtained from the general approach used in the present manuscript.

For those who got lost in the gory details of the physical chemistry I just discussed, just know that the theoretical approach in the present manuscript is, at least in part, inconsistent with obtaining the ~17% branching percentage (at 298 K) found for H-abstraction in the reaction of Cl + isoprene (Bedjanian et al., 1998, cited in the manuscript).

4. As Anonymous Referee #1 points out, hindered rotor corrections to rate constants may be important.

TECHNICAL CORRECTIONS

1. The GC temperature program and flow rate should be specified (at least in the Supplementary Material).
2. On page 5 where the absence of loss of test and reference compounds was verified in the dark and in the absence of oxalyl chloride, please specify the upper limit to the loss (e.g., < 4%). Similarly, specify the upper limit to the change in rate constant upon adding O₂ (and the partial pressure of O₂ used).
- 3a. The sample of 4-hexen-3-one is listed as >90% trans. The manuscript should specify whether the reported GC measurements were only of the trans isomer. Also, the manuscript should specify the cis/trans composition of 4-hexen-3-one as it appears in nature (if known). Every time the description of the calculations identifies the test compounds, they should specify trans (e.g., “*trans*-4-hexen-3-one” rather than “4-hexen-3-one”).
- 3b. Is the 5-hexen-2-one used in experiments all trans?
4. In the computational methodology, expand the acronyms CVT and SCT. The partition function of the reactant does not depend on *s*, as stated here. V_{MEP} should be specified as a potential energy **difference** (corrected for zero-point energy). The value of the reaction path degeneracy for each TS should be specified somewhere.
5. In Table 10, specify whether the experimental or theoretical rate constants used for Cl reactions with 4-hexen-3-one and 5-hexene-2-one. Also, add a second digit to the lifetimes with respect to reaction with OH, and only use two significant figures elsewhere.
6. Caption to Table 11. These are “percentages” not “ratios”.
7. Conformers:
 - Did the authors choose the conformers because they were the minimum energy conformers? If so, what efforts were made to verify this?
 - Two of the three test compounds are listed as having near-C_s symmetry, and probably should be treated as having C_s symmetry. This means that there are fewer unique transition states than listed (e.g., for 4-hexen-3-one TSs 8-10 are only two unique TSs).
8. Can Cl form a van der Waals complex with the π cloud of the carbonyl groups?
9. Both “test” and “sample” are used for the alkenones; please standardize terminology
10. In Table 1, some of the error bars don’t make sense, e.g., bottom of page 21 (298 K):
 - for 1,3 butadiene as a reference, the error bar on $k_{\text{test}}/k_{\text{ref}}$ is 25%, but the error bar on k_{test} is only 7%.
 - for isoprene as a reference, the error on the three individual values of $k_{\text{test}}/k_{\text{ref}}$ is on the order of 7-9%, and that should be reflected in the average value of $k_{\text{test}}/k_{\text{ref}}$.
 - for the final value of k_{test} averaged over multiple reference compounds, the error bar should be closer to 1.0 than 0.4 ($\times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$).
11. The Supporting Information is more complete than many, but it should also include absolute energies at 0 K, zero-point energies, and (ideally) H and G at 298 K. Also add

the CVT rate constant and tunneling corrections versus temperature for each reaction path for all three test molecules.

12. The Introduction does not reflect a thorough understanding of atmospheric chemistry and cites too few recent papers.
13. Page 6: use a lower case rather than upper case kappa for tunneling corrections.
14. The equations given for rate constants on page 6 have units of sec^{-1} . Please correct them.
15. On page 7, the results of Bedjanian et al. were at low pressure, not atmospheric pressure, although the rate constant was reported to be independent of pressure.
16. On page 7, lines 28 “10%” should be “16%”