

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.

GENERAL COMMENTS

R2Q1. 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.

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.

Table 1: Relative rate measurements for the reaction of Cl atoms with 4-hexen-3-one over the temperature range of 298-363K at 760 Torr in N₂ 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}) ±2σ	(k _{sample} /k _{reference}) Average±2σ	(k±2σ)×10 ⁻¹⁰ cm ³ molecule ⁻¹ s ⁻¹	(k±2σ)×10 ⁻¹⁰ cm ³ molecule ⁻¹ s ⁻¹	Lit. (k±2σ)×10 ⁻¹⁰ (cm ³ molecule ⁻¹ s ⁻¹) at 298K
298±2	1,3-butadiene	N ₂	760	1.55±0.21	1.54±0.27	5.10±0.81	5.55±1.31	3.00±0.58 Blanco et al.
				1.43±0.24				
				1.64±0.27				
	isoprene	N ₂	760	1.63±0.15	1.61±0.14	5.84±0.80		
				1.62±0.11				
				1.60±0.13				
	1-pentene	N ₂	760	1.12±0.12	1.21±0.19	5.71±0.62		
				1.09±0.13				
				1.33±0.10				
				1.33±0.10				
	isoprene	N ₂ – O ₂ (20)	760	1.57±0.14	1.59±0.11	5.74±0.18	5.74±0.18	
				1.61±0.11			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			5.61±0.25	
	isoprene	N ₂	500	1.59±0.11	1.57±0.10	5.67±0.18	5.67±0.18	
				1.55±0.12			5.67±0.18	
310±2	1,3-butadiene	N ₂	760	1.49±0.12	1.50±0.13	4.67±0.06	4.20±0.47	
				1.51±0.16				
	isoprene	N ₂	760	1.24±0.10	1.29±0.13	4.13±0.22		
				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	3.45±0.25	
				1.31±0.11				
	isoprene	N ₂	760	1.24±0.10	1.15±0.13	3.36±0.20		
				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	2.89±0.28	
				1.32±0.12				
	isoprene	N ₂	760	0.98±0.07	1.06±0.13	2.84±0.26		
				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	2.60±0.19	
				1.28±0.12				
	isoprene	N ₂	760	0.87±0.04	0.86±0.08	3.01±0.10		
				0.88±0.02				
				0.85±0.06				
	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 with reference 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})±2σ	(k _{sample} /k _{reference}) _{Average} ±2σ	(k±2σ)×10 ⁻¹⁰ (cm ³ molecule ⁻¹ s ⁻¹)	(k _{Average} ±2σ)×10 ⁻¹⁰ (cm ³ molecule ⁻¹ s ⁻¹)	Lit.k×10 ⁻¹⁰ (cm ³ molecule ⁻¹ s ⁻¹) at 298K
298±2	1,3-butadiene	N ₂	760	1.24±0.13	1.26±0.15	4.19±0.63	4.14±1.25	3.15±0.5 Blanco et al.
				1.26±0.10				
				1.29±0.11				
	isoprene	N ₂	760	1.18±0.09	1.09±0.20	3.95±0.97		
				1.14±0.10				
				0.97±0.16				
	1-pentene	N ₂	760	0.87±0.09	0.91±0.16	4.27±0.38		
				0.95±0.08				
				0.91±0.08				
	isoprene	N ₂ – O ₂ (20)	760	1.13 ±0.11	1.12±0.12	4.03±0.56	4.03±0.56	
				1.11±0.09				

	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 0.99±0.09 1.10±0.08	1.02±0.13	2.60±0.25		
									1-pentene	N ₂	760		
1,3-butadiene					N ₂ – O ₂ (20)	760	1.11±0.09 1.08±0.07					1.09±0.10	

R2Q2: 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.

Response: Both experimental and theoretical studies give a better understanding of the chemical reactions which are occurring in the troposphere. Experimentally, one can measure the global rate coefficient whereas theoretically, we can calculate the contribution of each reaction site towards its global rate coefficient and also gives the essential information about the reaction mechanism. In the present investigation, branching ratio calculations were performed using computationally obtained rate coefficients.

SPECIFIC COMMENTS ON EXPERIMENTS

R2Q3. 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 mJ cm⁻² 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.

Response: As mentioned in section 2.1, we have performed some preliminary tests before doing the experiments to check the influence of the secondary chemistry on title reactions. The reaction mixture (test molecule, reference compound and the precursor for Cl atom) was kept for 6 hours in dark which is more than the actual reaction time. The samples were analyzed in the GC at every half-an-hour and verified for any significant loss of the reactants and no such influence was observed. The sample mixture without the precursor (the test molecules and the reference compounds) was irradiated at 248 nm for 5 minutes, to verify the loss of the compounds due to direct photolysis. A maximum of 3 to 4% of the change in concentrations was observed, which indicates that neither the test molecules nor the reference compounds were dissociated by photolysis. A good way of confirming the secondary chemistry is via scavenging the radicals by adding oxygen. At room temperature and at extreme temperatures, oxygen was added to the reaction mixture and obtained rate coefficients are given in Tables 1 and 2. A maximum of 5% change was observed in the rate coefficients, which shows the negligible influence of secondary reactions due to the radicals formed in the test reaction.

The experiments were carried out with a repetition rate of 10 Hz at 248 nm wavelength and its fluence was maintained at 5-6 mJ cm⁻² pulse⁻¹. The typical concentrations of the reactant and

reference compounds were varied between $(4-6) \times 10^{16}$ molecules cm^{-3} and that of oxalylchloride was maintained between $(4-6) \times 10^{17}$ molecules cm^{-3} . This is added in the RMS.

R2Q4. 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.

Response: The experiments which were performed in presence of O_2 are incorporated for the reactions of Cl atoms with 4-hexen-3-one and 5-hexen-2-one in Tables 1 and 4 respectively in the RMS. The concentrations of test molecules and the reference compounds measured using Gas Chromatography (GC) at 1200, 1400, 1600, 1800 and 2000 pulses for every experiment are given in the revised supplementary material.

R2Q5. The literature values of the rate constant for Cl + isoprene and Cl + 1-pentene are only known up to 320K. 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.

Response: Rate coefficients for the reference reactions (Cl + 1-pentene and isoprene) are available only up to 320K. In the lack of availability of the reference rate coefficients up to 363K, the extrapolated rate coefficients were used in the measurements. In addition, the measurements were carried out using 1,3-butadiene as a third reference. Please refer to our response to R2Q1 of this reviewer for complete description.

R2Q6. 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.

Response: To know the importance of the Cl atom reactions, the atmospheric lifetimes of the test molecules were estimated with respect to their reactions with Cl atoms both in ambient conditions (1.00×10^3 molecules cm^{-3} , Singh et al., 1996) and marine boundary layer (1.30×10^5 molecules cm^{-3} , Spicer et al., 1998). In ambient conditions the lifetimes of 4-hexen-3-one, 5-hexen-2-one and 3-pentene-2-one are 8, 12 and 19 days respectively. In the marine boundary

layer the lifetimes of 4-hexen-3-one, 5-hexen-2-one and 3-pentene-2-one are estimated as 3.5, 5.3 and 8.7 hours respectively. Since the Cl atom reactions are important mainly in marine boundary layer and polluted urban areas where the Cl atom concentration reaches 1.3×10^5 atoms cm^{-3} , it was considered when compared with other oxidants in the Table 10. This is added in the atmospheric implications (section 3.8) of the RMS.

SPECIFIC COMMENTS ON CALCULATIONS

R2Q7. 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.

Response: 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. Hence, 6-31+G(d,p) basis set was used for single point calculations.

One of the composite method is G3MP2 and the obtained rate coefficients with G3MP2 are overestimated when compared with experimental and reported rate coefficients for the title reactions. However, with other level of theories and basis sets, we observed the Cl atom addition reactions are more dominant and showing negative temperature dependence over the studied temperature range for all the title reactions. We tried to optimize all the geometries with DFT and meta DFT methods such as B3LYP and M062X level of theories and were not successful in getting most of the transition states. Having this technical difficulty, the rate coefficients obtained at CCSD(T)/6-31+G(d, p)//MP2/6-311++G(d, p) level of theory were used to compared with the experimental and reported rate coefficients.

R2Q8. 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.

Response: We have checked the variational effects for all the three reactions and found that these addition channels are not having variational effects. As the reviewer rightly pointed out, we have measured the rate coefficients at the high pressure limits (1 atm. Pressure of N₂ and 298 to 363K). This is added in the RMS.

R2Q9. 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).

Response:

a) The allylic hydrogens are TS8, TS9 and TS10; TS6 and TS7; TS6, TS7 and TS8 in 4-hexen-3-one, 5-hexen-2-one and 3-penten-2-one respectively. These hydrogen abstractions from allylic sites are thermodynamically feasible (*c.f.* Tables 6, 7 and 8) and kinetically (*c.f.* Table 11 and Figures 12, 13 and 14) not favorable with low barrier heights, which are consistent with our earlier results (Walvalkar et al., 2016 and Vijayakumar et al., 2017).

b) The Cl atom addition followed by HCl elimination (roaming path) would have effect on the determination of the total rate coefficients of the title reactions. The HCl formation in the reaction of Cl atom with isobutene via roaming mechanism was observed by Chen et al. (DOI: 10.1038/srep40105) and experimental conditions was entirely different from the present study. The roaming path approach is completely different study from the present one.

Walavalkar, M. P., Vijayakumar, S., Sharma, A., Rajakumar B., Dhanya, S. Is H atom abstraction important in the reaction of Cl with 1-alkenes? J. Phys. Chem. A 120, 4096-4107, 2016.

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.

R2Q10. As Anonymous Referee #1 points out, hindered rotor corrections to rate constants may be important.

Response: 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 (cm³ molecule⁻¹ 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 _{Theory with HRcorrection}	3.60×10 ⁻¹⁰	5.47×10 ⁻¹⁰	2.38×10 ⁻¹⁰
k _{Experimental}	(5.55±1.31)×10 ⁻¹⁰	(4.14±1.25)×10 ⁻¹⁰	-
k _{Blanco <i>et al.</i>}	(3.00±0.58)×10 ⁻¹⁰	(3.15±0.50)×10 ⁻¹⁰	(2.53±0.54)×10 ⁻¹⁰

Table: Comparison of the theoretically obtained rate coefficients (cm³ molecule⁻¹ 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 _{Theory with HR correction}	k _{Theory}	k _{Theory with HR correction}	k _{Theory}	k _{Theory with HR correction}
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 HO₂ + CH₂NH: 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: OH+CH₂O, OH+CH₂CH₂, and OH+CH₂NH. J. Phys. Chem. A 119, 7578-7592, 2015.

TECHNICAL CORRECTIONS

R2Q11. The GC temperature program and flow rate should be specified (at least in the Supplementary Material).

Response: The following conditions were maintained during the GC analyses of the reaction mixtures.

Inlet temperature: 160°C

Pressure: 24.05 PSI

HP Plot Q Column flow: 1.96 ml min⁻¹

Pressure: 24.05 PSI

Oven temperature: 220 °C

Run time: 6 minutes

FID detector temperature: 240 °C

The above information is given in the revised supplementary material.

R2Q12. 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).

Response: The sample mixture without the precursor was irradiated at 248 nm for 5 minutes, to verify the loss of the compounds due to direct photolysis and a maximum of 3 to 4% of the change in concentrations was observed which indicates non-interference of the secondary chemistry on the title reactions. About 20 Torr of oxygen was added to the reaction mixture (maintained at 760 Torr) and the experiments were carried out at room temperature and at

extreme temperatures. The obtained rate coefficients are given in Tables 1 and 2. Maximum 5% change was observed in the rate coefficients which shows the negligible influence of secondary reactions due to the radicals formed in the test reaction. This is added in the RMS.

R2Q13. 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?

Response: 4-hexen-3-one exists in the form of trans (90%) and cis isomers (10%) in nature. Hence, we have used trans-4-hexen-3-one in our experiments. 5-hexen-2-one exists only in one conformation, which was used in present experiments. This is incorporated in the RMS.

R2Q14. In the computational methodology, expand the acronyms CVT and SCT. The partition function of the reactant does not depend on s , as stated here. VMEP 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.

Response: Acronyms CVT and SCT are expanded in introduction as Canonical Variational Transition state theory (CVT) with Small Curvature Tunneling (SCT) and have used as CVT and SCT throughout the text.

The partition function of the reactant does not depend on s . Hence, we have edited the sentence as “ ϕ^R and Q^{GT} are the partition functions of generalized reactant and transition state respectively”.

‘ s ’ is a reaction coordinate parameter that determines the location of the generalized transition dividing surface.

$V_{MEP}(s)$ is the potential along the reaction path at ‘ s ’ and the minimum energy pathways (MEP) was constructed with a gradient step size of 0.01.

For all the title reactions, all the transitions states are independent and the reaction path degeneracy is one ($\sigma=1$). This is added in the RMS.

R2Q16. 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.

Response: To calculate the lifetimes of test molecules, we have used present experimentally measured rate coefficients. The significant figures are corrected in the RMS as suggested.

R2Q17. Caption to Table 11. These are “percentages” not “ratios”.

Response: The word “ratios” is replaced with “percentages” in the RMS.

R2Q18. 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).

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.

In methyl group of the 4-hexen-3-one, three H-abstraction transition states (TS8-TS10) are there. Out of three, two transition states are having the similar energies (*c.f.* Tables 6, 7 and 8). Although they are having similar energies, we have considered all the transition states in the calculation of the total rate coefficients for all three reactions, as they are structurally different. Therefore, it may not be helpful if the molecule is considered to have C_s symmetry.

R2Q19. Can Cl form a van der Waals complex with the π -cloud of the carbonyl groups?

Response: There are possibilities for the formation of van der Waals complexes for transition states TS2 and TS7 in case of reaction R1; TS2 and TS5 in case of reaction R2; TS2 and TS5 in case of reaction R3. However, when we have optimized all these structures, we did not observe

any van der Waals complexes as the bond lengths are greater than 3.5 Å between Cl and cloud of the carbonyl group.

R2Q20. Both “test” and “sample” are used for the alkenones; please standardize terminology

Response: It was corrected and “test” was used throughout the RMS.

R2Q21. 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 ($\times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$).

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 $\pm 2\text{K}$) and pressure (within $\pm 1 \text{ Torr}$) 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 ($(k_{\text{sample}}/k_{\text{reference}})_{\text{Average}}$) 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: $\Delta k_{\text{test}} = k_{\text{test}} \times [(\Delta k_{\text{ref}}/k_{\text{ref}})^2 + (\Delta(k_{\text{test}}/k_{\text{ref}})/(k_{\text{test}}/k_{\text{ref}}))^2]^{1/2}$, where $(\Delta k_{\text{ref}}/k_{\text{ref}})$ and $\Delta(k_{\text{test}}/k_{\text{ref}})/(k_{\text{test}}/k_{\text{ref}})$ are the relative errors on k_{ref} and $k_{\text{test}}/k_{\text{ref}}$, respectively. At every temperature, the uncertainties in the averaged rate coefficients were calculated according to the equation: $\Delta k_{\text{average}} = k_{\text{average}} \times [(\Delta l/k_l)^2 + (\Delta m/k_m)^2 + (\Delta n/k_n)^2]^{1/2}$, 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.

R2Q22. 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.

Response: Absolute energies at 0K, zero-point energies and thermodynamic parameters such as enthalpies, Gibbs free energies and entropies were given in the revised supporting information along with CVT rate constants and tunneling corrections versus temperature for each reaction path of each reaction.

R2Q23. The Introduction does not reflect a thorough understanding of atmospheric chemistry and cites too few recent papers.

Response: Now, we have added the below given references, where the usage of laboratory studies on atmospheric chemistry were described in detail. The descriptions include atmospherically relevant processes which provides the fundamental information on climate change, urban air pollution, stratospheric ozone depletion and ecosystem health. This is added in the RMS.

Burkholder, J. B., Jonathan, P. D. A., Barnes, I., Roberts, J.M., Melamed, M. L., Ammann, M., Christopher, D.C., Annmarie, G.C., Lucy, J.C. and Crowley, J.N. et al. The essential role for laboratory studies in atmospheric chemistry, *Environ. Sci. Technol.*, 51, 2519-2528, 2017.

Ng, N. L.; Brown, S. S.; Archibald, A. T.; Atlas, E.; R.C, C.; Crowley, J. N.; Day, D. A.; Donahue, N. M.; Fry, J. L.; al, F. Nitrate radicals and biogenic volatile organic compounds: Oxidation, mechanisms and organic aerosol. *Atmos. Chem. Phys.* 17, 2103-2162, 2017.

Poschl, U.; Shiraiwa, M. Multiphase chemistry at the atmosphere-biosphere interface influencing climate and public health in the anthropocene. *Chem. Rev.* 115, 4440–4475, 2015.

West, J. J.; Cohen, A.; Dentener, F.; Brunekreef, B.; Zhu, T.; Armstrong, B.; Bell, M. L.; Brauer, M.; Carmichael, G.; Costa, D. L.; et al. What we breathe impacts our health: Improving understanding of the link between air pollution and health. *Environ. Sci. Technol.* 50, 4895–4904, 2016.

Liggio, J.; Li, S. M.; Hayden, K.; Taha, Y. M.; Stroud, C.; Darlington, A.; Drollette, B. D.; Gordon, M.; Lee, P.; Liu, P.; et al. Oil sands operations as a large source of secondary organic aerosols. *Nature* 534, 91–95, 2016.

R2Q24. Page 6: use a lower case rather than upper case kappa for tunneling corrections.

Response: Now lower case Kappa is used in the RMS.

R2Q25. The equations given for rate constants on page 6 have units of sec-1. Please correct them.

Response: corrected.

R2Q26. 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.

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

Bedjanian et al. have reported the temperature dependent rate coefficient for the reaction of isoprene with Cl atom in the temperature range of 233-320K and at low pressure.

R2Q27. On page 7, lines 28 “10%” should be “16%”

Response: Corrected.