Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-163, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 12 April 2017

Atmospheric Chemistry and Physics
Open Access
Discussions

Experimental and computational kinetics investigations for the reactions of Cl atoms with series of unsaturated ketones in gas phase

Siripina Vijayakumar, Avinash Kumar, and Balla Rajakumar*

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India.

*Address for correspondence: rajakumar@iitm.ac.in

http://chem.iitm.ac.in/faculty/rajakumar/

Abstract

Temperature dependent rate coefficients for the gas phase reactions of Cl atoms with 4-hexen-3-one and 5-hexen-2-one were measured over the temperature range of 298-363K relative to 1-pentene, 1,3-butadiene and isoprene. Gas Chromatography (GC) was used to measure the concentrations of the organics. The derived temperature dependent Arrhenius expressions are $k_{4\text{-hexen-3-one+Cl (298-363K)}} = (2.82\pm1.76)\times10^{-12}\exp[(1556\pm438)/T]$ cm^{3}molecule^{-1}s^{-1} and $k_{5\text{-hexen-2-one+Cl (298-363K)}} = (4.6\pm2.4)\times10^{-11}\exp[(646\pm171)/T]$ cm^{3}molecule^{-1}s^{-1}. The corresponding room temperature rate coefficients are $(5.54\pm0.41)\times10^{-10}$ cm^{3}molecule^{-1}s^{-1} and $(4.00\pm0.37)\times10^{-10}$ cm^{3}molecule^{-1}s^{-1} for the reactions of Cl atoms with 4-hexen-3-one and 5-hexen-2-one respectively. To understand the mechanism of Cl atom reactions with unsaturated ketones, computational calculations were performed for the reactions of Cl atoms with 4-hexen-3-one, 5-hexen-2-one and 3-penten-2-one over the temperature range of 275-400K using Canonical Variational Transition state theory (CVT) with Small Curvature Tunneling (SCT) in combination with CCSD(T)/6-31+G(d, p)//MP2/6-311++G(d, p) level of theory. Atmospheric implications, reaction mechanism and feasibility of the title reactions are discussed in this manuscript.

Key words

Unsaturated ketones, kinetics with Cl atoms, Canonical Variational Transition state theory (CVT) with Small Curvature Tunneling (SCT), Temperature dependent rate coefficients, Atmospheric life times.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-163, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 12 April 2017

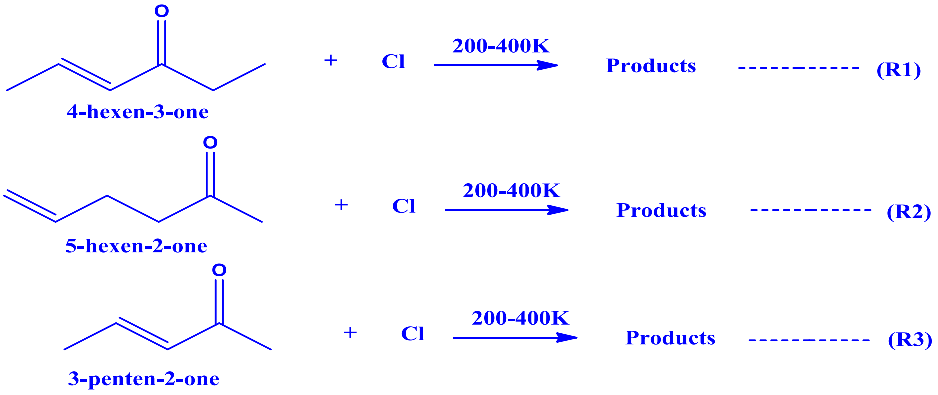
1. Introduction

In recent past, large amounts of hydrocarbons such as ketones, aldehydes, ethers, esters, alcohols, acids and aromatic compounds are being released into the atmosphere as they have wide usage in manufacturing of plastics, electronic components, polymers, textile and other industrial applications (Graedel et al., 1978). These hydrocarbons are removed from the atmosphere by several physical and chemical processes such as wet deposition, chemical degradation and photolysis. Further reactions of these compounds leads to the formation of secondary organic aerosols (SOAs) and photochemical smog (Derwent et al., 1996 and Hatakeyama et al., 1987) which effects the air quality, climate change and human health. Recent studies show that the global oxidation of biogenic volatile organic compounds contributing 90% of the SOAs in the atmosphere (Kanakidou et al., 2005).

Among all the hydrocarbons, ketones have received an abundant attention as they play an important role in the Earth's atmosphere. They form free radicals on reacting with atmospheric oxidizing species such as OH radicals, Cl atoms, NO_3 radicals and O_3 molecules. These free radicals are the important intermediates in the formation of aerosols and main sources for other oxidants such as ozone, peroxycarboxylic acids and peroxyacyl nitrates which can affect the oxidation capacity of the atmosphere (Calvert et al., 1987). In combustion chemistry, these ketones play an important role as they are formed as intermediates during the oxidation of oxygenated fuels and hydrocarbons at high temperatures (Rothamer et al., 2009). The end products of these carbonyl compounds are formaldehyde, acetaldehyde and acetone which contribute 40% of the ozone formation in polluted urban areas (Duan et al., 2008).

4-hexen-3-one, 5-hexen-2-one and 3-penten-2-one are being released into Earth's atmosphere by variety of plants from its leaves and by cooking waste (Karl et al., 2001; Tanchotikul et al., 1989 and Shimoda et al., 1995). These compounds are widely used in manufacturing of insecticides, fungicides and as solvents. Combustion of residential wood, burning of biomass and vegetation are the significant sources for releasing 4-hexen-3-one into the atmosphere. 4-hexen-3-one is an intermediate product in the synthesis of variety of perfumes (Wiley-VCH, 2011). As these compounds are released excessively via both anthropogenic and natural sources, they might exhibit certain impacts on the Earth's atmosphere. Therefore, as a first step, to understand the fate of these molecules in the troposphere, one should know the rate coefficients for their reactions with different atmospheric oxidants. In this attempt, Wang et al., 2010 measured the rate coefficients for the reactions of 5-hexen-2-one with OH radicals, O_3 molecules, and NO_3 radicals and reported them to be $k_{298K}=(4.49\pm1.02)\times10^{-11}$ $cm^3molecule^{-1}s^{-1}$, $k_{298K}=(9.17\pm0.15)\times10^{-18}$ $cm^3molecule^{-1}s^{-1}$ and $k_{298K}=(2.16\pm0.21)\times10^{-14}$ cm^3 $molecule^{-1}s^{-1}$ respectively. Blanco et al., 2012 measured the rate coefficients for the reactions of Cl atoms with 4-hexen-3-one, 5-hexen-2-one and 3-penten-2-one at room temperature and one atmospheric pressure and reported them to be $k_{298K}=$ $(3.00\pm$ $0.58)\times10^{-10}$ $cm^3molecule^{-1}s^{-1}$, $k_{298K}=(3.15\pm0.50)\times10^{-10}$ $cm^3molecule^{-1}s^{-1}$ and $k_{298K}=(2.53\pm0.54)$ $\times10^{-10}$ $cm^3molecule^{-1}s^{-1}$ respectively. Blanco et al.,[13] also measured the rate coefficients for the reactions of OH radicals with 4-hexen-3-one, 5-hexen-2-one and 3-penten-2-one and reported them to be $k=$ $(9.04\pm2.12)\times10^{-11}$ $cm^3molecule^{-1}s^{-1}$, $k=(5.18\pm1.27)\times10^{-11}$ $cm^3molecule^{-1}s^{-1}$ and $k=(7.22\pm1.74)\times10^{-11}$ $cm^3molecule^{-1}s^{-1}$ respectively at 298K and atmospheric pressure. Temperature and pressure dependent rate coefficients for the reactions of test molecules with Cl atoms are required to understand their atmospheric fate in urban polluted areas and marine boundary layers where the Cl atom concentrations are very high.

Till date, no data is available on the temperature dependence of the rate coefficients for the test molecules. In this study, the temperature dependent rate coefficients of the proposed reactions were measured. The global rate coefficients can be measured experimentally but theoretically the individual rate coefficients can be calculated for each and every reaction site, the complete potential energy surface i.e. how the reaction takes place from the reactant to product via different transition states. Thermodynamic parameters were calculated to know the feasibility of the reactions. Hence, computational calculations were performed for the reactions of Cl atoms with 4-hexen-3-one, 5-hexen-2-one and 3-penten-2-one using CVT/SCT in combination with CCSD(T)/6-31+G(d,p)//MP2/6-311++G(d,p) level of theory.



2.1. Experimental Methodology

Temperature dependent rate coefficients were measured for the title reactions using relative rate experimental technique. The complete experimental set up used in this study was described in our previous article (Vijayakumar et al., 2016). Experiments were carried out in a double walled Pyrex reaction chamber of 1250 cm^3 volume. Cl atoms were produced in situ by photolysis of oxalylchloride $(COCl)_2$ at 248 nm using an Excimer laser (Coherent Compex Pro). The experiments were carried out with a laser fluence of 5-6 mJ $pulse^{-1}$. Reaction mixture was photolyzed by 1200, 1400, 1600, 1800 and 2000 pulses and allowed for 20 minutes to equilibrate before analysis. Gas Chromatograph (GC, Agilent Technologies 7890B) coupled with Flame Ionization detector (FID) was used to measure the concentrations of test molecules and reference compounds. The GC was operated at optimized temperature and flow conditions to elute the test molecules with distinguishable retention times. HP plot Q column (30m× 0.320mm×20.0 μm, 19091P-Q04) was used for the analyses in the GC. 1-pentene, isoprene and 1,3-butadiene compounds were used as reference compounds. The temperature dependent rate coefficients for the reactions of 1-pentene (Coquet et al., 2000) and isoprene (Bedjanian et al., 1998) with Cl atom are available in the literature (*vide infra*) and therefore, they were used as reference compounds in the entire studied temperature range. However, only room temperature (298K, *vide infra*) rate coefficient is available in case of the reaction of 1,3-butadiene (Notario et al., 1997) with Cl atom and hence it was used in our studies as reference compound at 298 K alone. Before the reaction kinetics were investigated, some preliminary tests were performed to estimate the influence of wall effects. The reaction mixture containing the 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 was irradiated at 248 nm for 5 minutes, to verify the loss of the compounds due to direct photolysis and no loss was observed. To account for the influence of any secondary reactions, oxygen was added to the reaction mixture and the experiments were carried out at room temperature and at extreme temperatures. No change in the measured rate coefficients was observed for all the test reactions which shows the absence or negligible influence of secondary reactions due to the radicals formed in the test reaction.

Temperature dependent rate coefficients were measured from the decrease in concentrations of sample and reference compounds due to their reactions with Cl atoms using the standard relative rate expression given below.

$$\ln\left\{\frac{[sample]_0}{[sample]_t}\right\} = \frac{k_{sample}}{k_{reference}} \ln\{\frac{[reference]_0}{[reference]_t}\}$$

where $[\text{sample}]_0$, $[\text{sample}]_t$, $[\text{reference}]_0$ and $[\text{reference}]_t$ are the concentrations of the sample and reference compounds (obtained in GC analyses) at time '0' and 't' respectively. k_{sample} and $k_{\text{reference}}$ are the rate coefficients for their reactions with Cl atoms. The ratios of the rate coefficients $k_{\text{sample}}/k_{\text{reference}}$ were obtained by plotting $\ln([\text{sample}]_0/[\text{sample}]_t)$ versus $\ln([\text{reference}]_0/[\text{reference}]_t)$. Rate coefficients for title reactions were obtained by multiplying the slope with rate coefficient of the reference reaction at the same temperature.

Chemicals

1,3-butadiene (purity 99.5%, Praxair), 1-pentene (purity ≥98.5%, Aldrich), isoprene (purity 99%, Aldrich), 4-hexen-3-one (>90% predominantly trans, Aldrich), 5-hexene-2-one (Aldrich, 99%), oxalylchloride (purity 98%, Spectrochem), Nitrogen (99.995%, Indogas, Chennai), Oxygen (98%, Indo gas, Chennai). These compounds were further purified using freeze-pump-thaw method.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-163, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 12 April 2017

2.2. Computational Methodology

The geometries of reactants (4-hexen-3-one, 5-hexene-2-one and 3-penten-2-one), reactive complexes (RCs), transition states (TSs) and products (Ps) were optimized at MP2 (Moller et al., 1934) level of theory with different Pople's basis (Frisch et al., 1984) sets such as 6-31+G(d, p) and 6-311++G(d, p). Intrinsic reaction coordinates (IRCs) calculations for every reaction were performed at MP2/6-311++G(d, p) level of theory. Transition states were identified with one negative imaginary frequency and reactants, pre-reactive complexes and products were identified with zero imaginary frequencies. Single point energy calculations (Rodriguez et al., 2010) were carried out to get an accurate energy barrier heights at CCSD(T)/6-31+G(d, p) level of theory. All electronic structure calculations were performed using the Gaussian 09 programme suite (Frisch et al., 2010).

2.3. Kinetics

Temperature dependent rate coefficients were computed for the title reactions over the temperature range of 275-400K using CVT with SCT (Curtiss et al., 1999 and Gonzalez-Lafont et al., 1991) at CCSD(T)/6-31+G(d, p)//MP2/6-311++G(d, p) level of theory.

$$k^{GT}(T,s) = \sigma \frac{k_B T}{h} \left(\frac{Q^{GT}(T,S)}{\phi^R(T)}\right) \exp\left(\frac{-V_{MEP}(s)}{k_B T}\right)$$

$$k^{CVT}(T) = min_s k^{GT}(T,s) = k^{GT}[T, s^{CVT}(T)]$$

where k^{CVT} is the rate coefficient calculated using CVT and k^{GT} is the generalized rate coefficient, h= Planck's constant, σ is the reaction path degeneracy, T= temperature (in Kelvin), k_B is the Boltzmann constant, ϕ^R and Q^{GT} are the partition functions of a generalized reactant at 's' and transition state respectively. S^{CVT} is the reaction coordinates of the canonical variational transition state dividing surface. $V_{MEP}(s)$ is potential energy of generalized TS at 's'. The tunneling corrected rate coefficients ($k^{CVT/SCT}$) were obtained by multiplying k^{CVT} and a temperature dependent transmission coefficient $K^{CVT/SCT}$(T).

$$k^{CVT/SCT}(T) = K^{CVT/SCT}(T) k^{CVT}(T)$$

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-163, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 12 April 2017

3. Results and Discussion

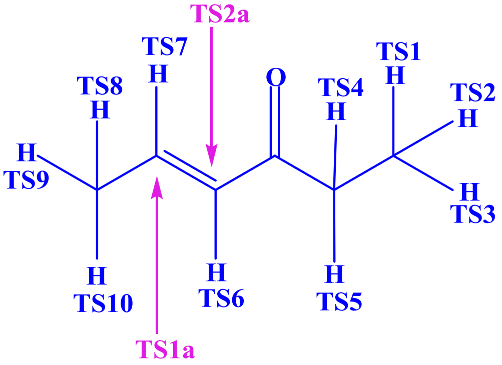
3.1. Reaction of Cl atoms with 4-hexen-3-one

3.1.1. Experimental

Temperature dependent rate coefficients for the reaction of Cl atoms with 4-hexen-3-one were measured over the temperature range of 298-363K relative to 1-pentene (Coquet et al., 2000), isoprene (Bedjanian et al., 1998) and 1,3-butadiene (Notario et al., 1997). The rate coefficient for the reaction of Cl atoms with 1,3-butadiene was used in present investigation which was measured by Notario et al. by using laser photolysis-resonance fluorescence technique and reported it to be k= (3.48 ±0.10) $\times 10^{-10}$ $cm^3 molecule^{-1} s^{-1}$ at 298K. 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 atmospheric pressure. These rate coefficient were measured using discharge flow – mass spectrometric method and reported it to be $k_{233\text{-}320K}$= $(6.7\pm2.0)\times10^{-11}$ exp[(485±85)/T] $cm^3 molecule^{-1} s^{-1}$. Coquet et al. have investigated the temperature dependent rate coefficient for the reaction of 1-pentene with Cl atom in the temperature range of 283-323K and at atmospheric pressure. These rate coefficients were measured with reference to n-hexane using relative rate method and reported it to be, $k_{283\text{-}323K}$= $(4.0\pm2.2)\times10^{-11}$ exp[(733±288)/T]cm^3 $molecule^{-1} s^{-1}$. These rate coefficients were used in the present investigation. As the temperature dependent rate coefficients for 1,3-butadiene are not available, the measurements using it were restricted to the room temperature (298K) only. However, isoprene and 1-pentene were used as reference compounds in the entire studied temperature range. Rate coefficients were measured at 298, 310, 330, 350 and 363K. The plot of relative decrease in the concentration of 4-hexen-3-one due to its reaction with Cl atoms relative to 1-pentene, 1,3-butadiene and isoprene is shown in Figure 1. The behavior of the relative decrease of the reactant was found to be linear through origin, explains the non-interference of the secondary chemistry on the reaction. The rate coefficients measured for the reaction of 4-hexen-3-one are given in Table 1. At room temperature, the obtained rate coefficients for the reaction R1 relative to 1-pentene, 1,3-butadiene and isoprene are very close to each other (maximum difference found was about 10%) and therefore, they were averaged and obtained the rate coefficient $k_{R1-298K}^{Expt}$=$(5.54\pm0.41)\times10^{-10}$ $cm^3 molecule^{-1} s^{-1}$. This rate coefficient at 298K is

45% larger than the theoretically calculated rate coefficient ($k_{R1-298K}^{Theory}$= 3.66×10^{-10} cm^{3}molecule^{-1}s^{-1}) *vide infra* and, also the one reported by Blanco et al. at 298K, (3.0±0.5)×10^{-10} cm^{3}molecule^{-1}s^{-1}. May be 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. Several groups have measured the rate coefficients of Cl atom reactions with unsaturated hydrocarbons at room temperature (298K), but only two temperature dependent rate coefficients (Cl + 1-pentene (Coquet et al., 2000) and Cl + isoprene (Bedjanian et al., 1998)) are available in literature whose rate coefficients are close to the rate coefficients of the title reaction at the temperatures across the study. Hence these two reference compounds were used in the present investigation. The obtained rate coefficients relative to 1-pentene and isoprene were averaged across the studied temperature range and depicted in Table 1. The obtained averaged rate coefficients were used to fit the temperature dependence by linear least squares method and is given in Figure 2. The derived temperature dependent Arrhenius expression for the reaction R1 is $k_{R1-(298-363K)}^{Expt}$ = (2.82±1.76)×10^{-12}exp[(1556±438)/T] cm^{3} molecule^{-1}s^{-1}.

3.1.2. Computational



Structure 1: 4-hexen-3-one

Geometries of the reactant, pre-reactive complexes, transition states and products were optimized at MP2/6-311++G (d, p) level of theory and shown in Figure 3. In the reaction of Cl atoms with 4-hexen-3-one, twelve (two addition channels and ten abstraction channels) transition states were identified. Addition transition states were represented by TS1a (adjacent to the –CH$_3$ group) and TS2a (adjacent to the –C=O group) and hydrogen abstraction channels were represented by TS1 to TS10 as shown in the structure 1. The Cl atom addition on double bond at TS1a and TS2a lead to the formation of secondary alkyl radicals Pla and P2a respectively. In hydrogen abstraction reactions, the –C-H bond length was elongated from 16% to 40% when compared with the normal –C-H bond length in the test molecule. The energies of all the stationary points were refined at CCSD(T)/6-31+G(d, p) using the optimized geometries obtained at MP2/6-311++ G(d, p) level of theory. Thus refined energies were used in dual level CVT calculations to compute the rate coefficients for the reaction over the temperature range of 275-400K. The potential energy diagram for reaction R1 is given in the Figure 4. From this Figure, it is very clear that the addition transition states (TS1a and TS2a) are submerged and therefore, these two channels would contribute maximum to the global rate coefficient. The pre-reactive complexes for these submerged channels were identified and used in the calculations. The global rate coefficient for the reaction R1 was calculated by linear summation of the individual rate coefficients viz.

$$k_{global} = k_{TS1a} + k_{TS2a} + k_{TS1} + k_{TS2} + k_{TS3} + k_{TS4} + k_{TS5} + k_{TS6} + k_{TS7} + k_{TS8} + k_{TS9} + k_{TS10}$$

The rate coefficient for the reaction R1 at 298K was calculated to be $k_{R1-298K}^{Theory} = 3.66\times10^{-10}$ $cm^3molecule^{-1}s^{-1}$. It should be noted that the theoretically calculated rate coefficient is in excellent agreement with the one reported by Blanco et al. at 298K, $(3.0\pm0.5)\times10^{-10}$ $cm^3molecule^{-1}s^{-1}$. The computed rate coefficients were used to fit the Arrhenius equation by linear least squares method and is given in Figure 2 along with the experimentally measured ones. The theoretically obtained temperature dependent rate coefficient for the reaction R1 is $k_{R1-(275-400K)}^{Theory} = (1.41\pm0.13)\times10^{-12}\exp[(1663 \pm57)/T]$ $cm^3molecule^{-1}s^{-1}$. The activation energies predicted by both theory and experiment seems to be very close to each other. However, the experimentally obtained pre-exponential factor is twice that of the one estimated by theory. Obviously, the trends of the rate coefficients are identical but the intercept, which is essentially the pre-exponential factor.

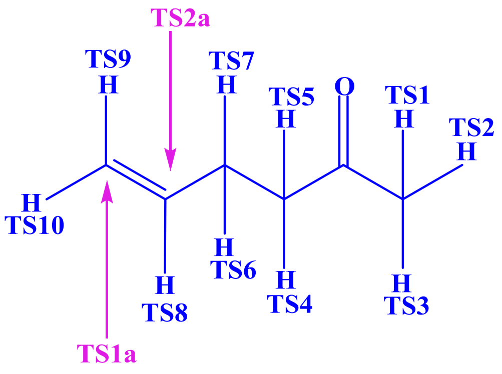
3.2. Reaction of Cl atoms with 5-hexene-2-one

3.2.1. Experimental

Rate coefficients were measured for the reaction of Cl atoms with 5-hexene-2-one over the temperature range of 298-363K relative to 1-pentene (Coquet et al., 2000) and isoprene

(Bedjanian et al., 1998). The plot of relative decrease in the concentration of 5-hexen-2-one due to its reaction with Cl atoms relative to 1-pentene and isoprene is shown in Figure 5. The linear behavior of the loss through the origin ascertains the non-influence of the secondary/radical chemistry. This was further checked by carrying out the reaction in the presence of excess oxygen at extreme temperatures of this study and no change in the measured rate coefficients was noticed. For the present reaction R2, the rate coefficients were measured at 298, 310, 330, 350 and 363K and they are tabulated in Table 4. The rate coefficients measured at 298 K with 1-pentene and isoprene as reference compounds differ by 12% and at 363K they are found to be same. As the difference falls well within the experimental uncertainties due to the usage of different experimental methods in determining the reference rate coefficients by various groups, they were averaged in our study. The average rate coefficient for the reaction R2 at 298K in the present study is obtained to be $k_{R2-298K}^{Expt}$=(4.0±0.3)×10^{-10} $cm^3molecule^{-1}s^{-1}$. The measured rate coefficient is reasonably in good agreement with the reported one by Blanco et al. at 298 K, (3.15±0.5)×10^{-10} $cm^3molecule^{-1}s^{-1}$. Thus an averaged rate coefficient at all the temperatures was used to fit the Arrhenius equation and is shown in the Figure 6 along with the available rate coefficients for this reaction. The temperature dependent rate coefficient for the reaction R2 is obtained to be $k_{R2-(298-363K)}^{Expt}$ = (4.6±2.4)×10^{-11} exp[(646±171)/T] $cm^3molecule^{-1}s^{-1}$.

3.2.2. Computational



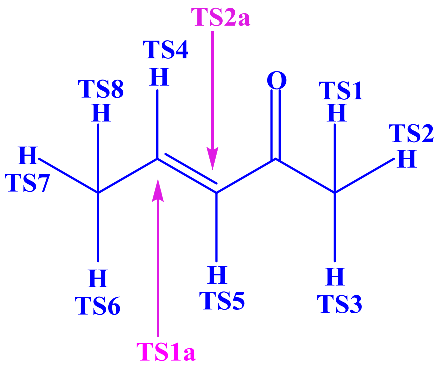
Structure 2: 5-hexen-2-one

The optimized geometries of the reactant, pre-reactive complexes, transition states and products are shown in Figure 7. In 5-hexen-2-one, two addition channels namely TS1a (terminal carbon) and TS2a (middle carbon) and abstraction channels TS1 to TS10 were found. As shown in the structure 2, addition transition states are represented by suffix ‘a’ and the transition states for hydrogen abstractions are labeled from TS1 to TS10 as identified above. The Cl atom addition across the double bond via transition states TS1a and TS2a forms secondary and primary radicals (P1a and P2a) respectively. Hydrogen abstraction reactions form products P1 to P10 via TSs TS1 to TS10 respectively. In case of hydrogen abstraction reactions, the leaving –C-H bond was stretched up to 30 to 41% when compared with normal -C-H bond length in the substrate. The stationary point energies were refined at CCSD(T)/6-31+G(d, p) using the optimized geometries obtained at MP2/6-311++G(d, p) level of theory. Thus refined energies were used in dual level CVT calculations to compute the rate coefficients for the reaction over the temperature range of 275-400K. The potential energy surface for this reaction is given in Figure 8. The contribution from the addition channels via transition states TS1a and TS2a is expected to be maximum and they are submerged channels. The corresponding pre-reactive complexes were also identified for these submerged reaction channels and were used in the rate coefficient calculations. As explained in the reaction R1, the global rate coefficient for reaction R2 was obtained by linear summation of rate coefficients for the individual channels. The rate coefficient for reaction R2 at 298K was calculated to be$k_{R2-298K}^{Theory}$= 5.56×10^{-10} cm^{3}molecule^{-1}s^{-1}. Theoretically calculated rate coefficient is larger by 45% when compared with the reported one by Blanco et al. at 298K, (3.15±0.5)×10^{-10} cm^{3}molecule^{-1}s^{-1}. Also, it is larger than the experimentally measured one by 22%. May be this is due to the uncertainties associated with the submerged transition states and theoretically calculated pre-exponential factors. Here it should be noted that the uncertainties in the calculated energies of adducts and transition states can critically effect the calculated rate coefficients. On the other hand, the pre-exponential factor which depends upon the partition functions of reactants and transition states are estimated in the calculations. The computed rate coefficients were used to fit the Arrhenius equation by linear least squares method and is given in Figure 6 along with the experimentally measured ones. The theoretically obtained temperature dependent rate coefficient for the reaction R2 is $k_{R2-(275-400K)}^{Theory}$ = (3.20±0.27)×10^{-12}exp[(1535±24)/T] cm^{3} molecule^{-1}s^{-1}. The activation energy for the reaction R2 estimated by theory is double than that of experimentally derived one. The pre-exponential factor estimated theoretically is lower than the experimentally derived one by an order of magnitude.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-163, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 12 April 2017

3.3. Reaction of Cl atoms with 3-penten-2-one

Although no data is available on the concentration of 3-penten-2-one in the atmosphere, the concentration may not be insignificant as the source is biomass. Therefore, measurement of the kinetics of the oxidation is useful. However, the vapor pressure of this compound is very less (less than a Torr at 298K). Therefore, experiments were not performed for this molecule. To understand the mechanism of oxidation of series of unsaturated ketones, 3-penten-2-one was also studied using computational methods along with 4-hexen-3-one and 5-hexen-2-one.



Structure 3: 3-penten-2-one

The optimized (MP2/6-311++G(d, p)) geometries of reactant (3-penten-2-one), pre-reactive complexes, transition states and products are shown in Figure 9. In 3-penten-2-one, two addition transition states namely TS1a and TS2a and eight hydrogen abstraction channels namely TS1 to TS8 were identified and are shown in the structure 3. As shown in potential energy level diagram Figure 10, Cl atom addition at TS1a and TS2a leads to the formation of secondary radicals P1a and P2a respectively. The transition states for the addition channels are submerged and the corresponding pre-reactive complexes were optimized at the same level of theory. The reaction is dominated by the addition pathways. During hydrogen abstraction reactions, the leaving –C-H bond was elongated from 16% to 34% when compared with normal -C-H bond in the reactant. The energies of all the stationary points were refined at CCSD(T)/6-31+G(d, p) using the optimized geometries obtained at MP2/6-311++G(d, p) level of theory. The refined energies were used in dual level CVT calculations to compute the rate coefficients for the reaction R3 over the temperature range of 275-400K. The global rate coefficient was obtained by summing the rate coefficients of individual pathways. The rate coefficient of the reaction R3 at 298 K was obtained to be $k_{R3-298K}^{Theory}$= 2.40×10^{-10} cm^{3}molecule^{-1}s^{-1}. Theoretically calculated rate coefficient shows the very good agreement with the reported one by Blanco et al. at 298K, (2.53±0.54)×10^{-10} cm^{3}molecule^{-1}s^{-1}. The calculated global rate coefficients were used to get the temperature dependence of the reaction R3 and derived Arrhenius expression is $k_{R3-(275-400K)}^{Theory}$ = (2.5±0.2)×10^{-12}exp [(1363±26)/T] cm^{3}molecule^{-1}s^{-1}. Arrhenius plot is shown in Figure 11 which shows negative temperature dependence over the studied temperature range.

3.4. Addition vs abstraction

As mentioned in the discussions of each reactions, the addition pathways contribute more towards the global rate, as all the corresponding transition states are submerged ones. The observed negative temperature dependence for the studied reactions R1, R2 and R3 is due to the stabilized submerged transition states. In a review on the reactions of unsaturated molecules with Cl atoms, (Taatjes, 1999) concluded that negative temperature dependence for the addition of Cl atoms across the double bond to be the most favourable pathway. In present investigation, for the reactions of Cl atoms with 4-hexen-3-one, 5-hexen-2-one and 3-penten-2-one have shown negative temperature dependence which is in consistent with the findings of Taatjes, 1999.

The contributions of the abstraction channels are negligible when compared to the addition channels. The temperature dependence of branching ratios of all the three reactions are given in Figures 12, 13 and 14. It is obvious from these Figures that both the addition channels across the double bond contribute maximum to the reaction. An abstraction channels seem to have a negligible contribution to the reaction in the studied temperature range. However, it should be noted that, the contribution of abstraction seems to be increasing with the temperature. The trends of the addition rate coefficients in case of the compounds containing double bonds adjacent to the C=O group (4-hexen-3-one and 3-pentene-2-one) were observed to follow similar trends. The rate coefficients for the addition of Cl atom at α position to C=O bond in case of both the molecules via transition state TS2a were observed to be increasing with the temperature. However, the rate coefficients for the addition at β position to C=O bond were observed to be decreasing with the increase in temperature. In both these molecules, β carbon is connected to CH_3 group, which is an electron donating group. The C-C bond rotation will be more favorable at higher temperatures, which would lead to elongation of the bond and therefore, the influence of the electron donating group reduces with the increase in temperature. Consequently, the transition state for the addition at β position would become "tight". In other words, the activation barrier height would increase and therefore, rate coefficient would decrease. In case of 5-hexen-2-one, due to the additional two CH_2 groups between double bond and C=O group, and the absence of CH_3 group at the terminal carbon, the above said influence will not play any role. And therefore, it is expected that, the addition across the double bond via transition states TS1a and TS2a should go with almost equal rates. This can be seen in the branching ratio plot for reaction R2.

3.5. Reactivity trend

The rate coefficients for the reactions of Cl atoms, OH and NO_3 radicals (Atkinson et al., 2003; Smith et al., 1996; Holloway et al., 2005; Neeb et al., 1998 and Canosa-Mas et al., 2005) with analogous molecules are given in Table 9. From Table 9, it is very clear that for the reactions of Cl atoms with unsaturated compounds, from propene to 1-pentene there is an increment in the rate coefficient due to insertion of two $-CH_2-$ groups. A significant drop in the rate coefficients for the reaction of Cl atoms, OH and NO_3 radicals was observed with insertion of –C=O group into the alkene. By insertion of $-CH_2$ group, the rate coefficient is increased from 3-buten-2-one to 3-penten-2-one by factor of 1.5 and from 3-penten-2-one to 4-hexen-3-one by factor of 1.2 which indicates that the reactivity increases by insertion of electron donating group ($-C_2H_4-$) whereas it decreases with insertion of a strong deactivating group (-C=O). The same trend can be observed for the reaction with NO_3 radicals that is insertion of $-C_2H_4-$ group into propylene to give 1-pentene increases the reactivity by a factor of 1.6 and insertion of C=O group into 1-pentene to give 5-hexen-2-one decreases the reactivity by a factor of 1.5. The similar effects are observed for the reactions of these compounds with OH radicals.

In case of OH radical reactions, $–C_2H_4$ group is inserted into 3-buten-2-one to give 5-hexen-2-one which increases the reactivity of 5-hexen-2-one. The α-substitution with two methyl groups in 5-hexen-2-one to give 6-methyl-5-hepten-2-one increases the reactivity of 5-hexene-2-one which indicates that the preferential electrophilic addition mechanism for OH reactions. Structure Activity Relations (SAR) (Kwok et al., 1995 and Mellouki et al., 2003) also supports this mechanism and according to SAR the reaction of Cl atoms and OH radicals with these unsaturated ketones proceeds via addition across the double bond as a predominant channel and only 15% accounts for hydrogen abstraction.

4-hexen-3-one (C_6H_{10}) and 5-hexen-2-one (C_6H_{10}) are structural isomers but the experimentally measured rate coefficient in present investigation for the reaction of Cl atoms with 4-hexen-3-one ($(5.54\pm0.41)\times10^{-10}$ $cm^3molecule^{-1}s^{-1}$) is higher than the reaction with 5-hexen-2-one ($(4.0\pm0.3)\times10^{-10}$ $cm^3molecule^{-1}s^{-1}$). The same trend was observed by Blanco et al. in the case of OH radical reactions. The rate coefficient for the reaction of 4-hexene-3-one with OH (9.04×10^{-11} $cm^3molecule^{-1}s^{-1}$) is higher than the rate coefficient for the reaction with 5-hexene-2-one (5.18×10^{-11} $cm^3molecule^{-1}s^{-1}$). Moreover, the double bond in 4-hexen-3-one is in conjugation with carbonyl group and upon Cl atom addition across double bond forms more stable radical which makes 4-hexen-3-one to be more reactive than the 5-hexen-2-one.

3.6. Feasibility of a reaction

To understand the feasibility and spontaneity of the reactions R1, R2 and R3 in terms of thermodynamic parameters, standard Gibb's free energies, enthalpies and entropies were calculated at MP2/6-311++G (d, p) level of theory and are given in Tables 3, 5 and 8. From these Tables, it is very clear that the Cl atom addition reactions are more favorable than hydrogen abstraction reactions which are in consistence with our findings using kinetic parameters (cf section 3.4). In reaction R1 (4-hexen-3-one + Cl), addition through TS1a and TS2a are equally spontaneous and exothermic. In case of reaction R2 (5-hexen-2-one + Cl) also, the addition of Cl atom through TS1a and TS2a are equally spontaneous and exothermic. The same trend was observed in case of reaction R3 (3-penten-2-one + Cl) as well.

As far as the abstraction of hydrogen channels are considered, all of them were found to be endothermic. Among all the possible hydrogen abstraction channels, abstraction of hydrogens attached to olefinic carbon are more endothermic. From Tables 3, 5 and 8, it is clear that there is a sudden jump in the ΔH^0 values for these channels (given with BOLD fonts, TS6 and TS7 in R1; TS8, TS9 and TS10 in R2; and TS4 and TS5 in case of R3 reactions).

3.7. Degradation mechanism

The reactions of unsaturated compounds with Cl atoms mainly proceeds via initial addition to the C=C bond (s) which is analogous to the other atmospheric oxidants such as OH, NO_3 and O_3 (Atkinson et al., 2003). In the product analysis of OH initiated reaction with double bonded molecule such as isoprene, Atkinson et al., 2003 has observed addition products like methyl vinyl ketone, HCHO, methacrolein, 3-methylfuran and C5-hydroxycarbonyls; and abstraction products like 1,4-hydroxyaldehyes with loss of water at room temperature and atmospheric pressure. In case of NO_3 radicals (Canosa-Mas et al., 2005), they undergo addition reactions and at low pressure, they form chemically activated nitrooxyalkyl radical and can decompose to an oxirane and NO_2 in competition with collisional stabilization. Similarly, reaction of O_3 with unsaturated molecules proceed via initial addition which forms primary ozonide, which further decompose to form Criegee intermediates (Neeb et al., 1998) via two different pathways.

The oxidation mechanism is proposed for one test molecule (5-hexen-2-one) based on the above observations and is given in Figure 15. The reactions of Cl atoms with test molecules occur primarily via addition across double bond to form chloroalkyl radicals. When these chloroalkyl radicals reacts with O_2 yields chloroalkyl peroxy radicals and in presence of NO_x, these chloroalkyl peroxy radicals form chloroalkoxy radicals. Finally, they form carbonyl compounds as end products.

3.8. Atmospheric implications

These unsaturated ketones would be degraded in the atmosphere due to their reactions with oxidants such as OH radicals, Cl atoms, NO_3 radicals and O_3 molecules. Therefore, cumulative atmospheric life times of 4-hexen-3-one, 5-hexen-2-one and 3-pentene-2-one with respect to OH radicals, Cl atoms, NO_3 radicals and O_3 molecules were calculated using the following equation

$$\frac{1}{\tau_{\mathrm{eff}}} = \frac{1}{\tau_{\mathrm{OH}}} + \frac{1}{\tau_{\mathrm{Cl}}} + \frac{1}{\tau_{\mathrm{O_3}}} + \frac{1}{\tau_{\mathrm{NO_3}}}$$

where τ_{eff} is the cumulative lifetime of the chemical species, τ_{OH}, τ_{Cl}, τ_{O3} and τ_{NO3} are rate coefficients for the reactions of test molecules with OH radicals, Cl atoms, O_3 and NO_3 radicals respectively. The global atmospheric concentrations used in present investigation are 2×10^6

radical cm^{-3}, 5×10^{8} radical cm^{-3} and 7×10^{11} molecules cm^{-3} for OH radical, NO_3 radicals and ozone respectively (Atkinson, 2000) and depicted in Table 10. 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} was considered when compared with other oxidants in the Table 10. From Table 10, it is very clear that the reactions of Cl atoms with test molecules are much faster (in the order of 10^{-10} cm^{3} molecule^{-1} s^{-1}) when compared with the reactions of OH radicals (in the order of 10^{-11} cm^{3} molecule^{-1} s^{-1}) and NO_3 radicals (in the order of 10^{-14} cm^{3} molecule^{-1} s^{-1}) and O_3 molecules (in the order of 10^{-17} cm^{3} molecule^{-1} s^{-1}). However, the atmospheric degradation of these ketones due to their reactions with Cl atoms are less when compared with OH radicals. This is because of lower concentrations of Cl atoms when compared with that of OH radicals in the Earth's atmosphere. However, the cumulative lifetimes of these test molecules are few hours. As these molecules are short lived they would not contribute to global warming in any time horizons.

4. Conclusions

In this study, reactions of Cl atoms with 4-hexen-3-one, 5-hexen-2-one and 3-penten-2-one were investigated (Reactions labeled R1, R2 and R3 respectively). 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) basis sets. 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 these addition reactions are more feasible and spontaneous. 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.

Supporting information:

The optimized parameters for the reactants, pre-reactive complexes, transition states and products are given in Tables S-1-1 to S-5-22 and the vibrational frequencies are given in Tables S-2-1 to S-6-4 for the reactions of Cl atoms with 4-hexen-3-one, 5-hexen-2-one and 3-penten-2-one.

Acknowledgement

The authors cordially thank the Department of Science and Technology (DST), Government of India, for the financial support. We also thank Mr.V.Ravichandran, High Performance Computing Environment (HPCE), IITMadras for the help in providing the computational resources to carry out the calculations.

References

Atkinson, R. and Arey, J.: Atmospheric degradation of volatile organic compounds, Chem.Rev., 103, 4605-4638, 2003.

Atkinson, R.: Atmospheric chemistry of VOCs and NO_x. Atmos. Environ. 34, 2063-2101, 2000.

Bedjanian, Y., Laverdet, G. and Bras., G. L.: Low pressure study of the reaction of Cl atoms with isoprene, J. Phys. Chem. A, 102, 953-959, 1998.

Blanco, M.B., Barnes I. and Wiesen, P.: Kinetic investigation of the OH radical and Cl atom initiated degradation of unsaturated ketones at atmospheric pressure and 298K, J.Phys.Chem. A 116, 6033-6040, 2012.

Calvert, J.G. and Madronich, S.: Theoretical study of the initial products of the atmospheric oxidation of hydrocarbons, J.Geophys. Res. 92, 2211-2220, 1987.

Canosa-Mas, C.E., Flugge, M.L., King, M.D. and Wayne, R.P.: An experimental study of the gas phase reaction of the NO_3 radical with α, β-unsaturated carbonyl compounds, Phys. Chem. Chem. Phys. 7, 643-650, 2005.

Coquet, S. and Ariya, P.A.: Kinetics of the gas-phase reactions of Cl atom with selected C_2-C_5 unsaturated hydrocarbons at 283 < T < 323 K. Int. J. Chem. Kinet, 32, 478-484, 2000.

Curtiss, L.A., Redfern, P.C., Raghavachari, K, Rassolov, V. and Pople, J.A.: Gaussian-3 theory using reduced Moller-Plesset order, J.Chem.Phys. 110, 4703-4709, 1999.

Derwent, R.G., Jenkin M.E. and Saunders, S.: Photochemical ozone creation potentials for a large number of reactive hydrocarbons under European conditions, Atmos.Environ., 30, 181-199, 1996.

Duan, J.C., Tan, J.H., Yang, L., Wu S. and Hao, J.M.: Concentration, sources and ozone formation potential of volatile organic compounds (VOCs) during ozone episode in Beijing, Atmos. Res. 88, 25-35, 2008.

Frisch, M.J., Pople, J.A. and Binkley, J.S.: Self-consistent molecular orbital methods 25. Supplementary functions for Gaussian basis sets, J.Chem. Phys., 80, 3265-3269, 1984.

Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Scalmani, G., Barone, V., Mennucci, B. and Petersson, G.A.; et al. Gaussian 09, Revision B.01.; Gaussian, Inc.: Wallingford, CT, 2010.

Gonzalez-Lafont, A., Truong, T.N. and Truhlar, D.G.: Interpolated variational transition state theory: practical methods for estimating variational transition state properties and tunneling contributions to chemical reaction rates from electronic structure calculations, J. Chem. Phys. 95, 8875−8894, 1991.

Graedel, T.E.: Chemical Compounds in the Atmosphere, Academic Press, New York, 1978.

Hatakeyama, S., Ohno, M., Weng, J., Takagi H. and Akimoto, H.: Mechanism for the formation of gaseous and particulate products from ozone-cyclo alkene reactions in air-Quantitative analysis of particulate products and the reaction mechanism, Environ. Sci. Technol., 21, 52–57, 1987.

Holloway, A.L., Treacy, J., Sidebottom, H., Mellouki, A., Daele, V., Bras, G.L. and Barnes, I.: Rate coefficients for the reactions of OH radicals with the keto/enol tautomers of 2,4-pentadione and 3-methyl-2,4-pentanedione, allyl alcohol and methyl vinyl ketone using the enols and methyl nitrite as photolytic sources of OH, J. Photochem. Photobiol. A Chem., 176, 183-190, 2005.

Kanakidou, M., Seinfeld, J.H., Pandis, S.N., Barnes, I., Dentener, F.J., Facchini, M.C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C.J., Swietlicki, E., Putaud, J.P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G.K., Winterhalter, R., Myhre, C.E.L., Tsigaridis, K., Vignati, E., Stephanou, E.G. and Wilson, J.: Organic aerosol and global climate modeling: a review, Atm. Chem. Phys., *5*, 1053–1123, 2005.

Karl, T., Fall, R., Jordan. A. and Lindinger, W.: On-line analysis of reactive VOCs from urban lawn mowing, Environ. Sci. Technol., 35, 2926−2931, 2001.

Kwok, E.S.C. and Atkison, R.: Estimation of hydroxyl radical reaction rate constants for gas phase organic compounds using a structure-reactivity relationship: An update, Atmos. Environ. 29, 1685-1695, 1995.

Mellouki, A., Bras G. L., and Sidebottom, H.: Kinetics and mechanisms of the oxidation of oxygenated organic compounds in the gas phase. Chem. Rev. 103, 5077-5096, 2003.

Moller, C. and Plesset, M. S.: Note on an approximation treatment for many-electron systems, Phys. Rev., 46, 618−622, 1934.

Neeb, P., Kolloff, A., Koch, S. and Moortgat, G.K.: Rate constants for the reactions of methylvinyl ketone, methacrolein, methacrylic acid and acrylic acid with ozone, Int. J. Chem. Kinet., 30, 769-776, 1998.

Notario, A., Lebras, G. and Mellouki, A.: Kinetics of C1 atom reactions with butadienes including isoprene, Chem. Phys. Lett., 281, 421-425, 1997.

Rodriguez, A., Rodriguez, D., Garzon, A., Soto, A., Aranda A. and Notario, A.: Kinetics and mechanism of the atmospheric reactions of atomic chlorine with 1-penten-3-ol and (Z)-2-penten-1-ol: an experimental and theoretical study, Phys. Chem. Chem. Phys., *12*, 12245–12258, 2010.

Rothamer, D.A., Snyder, J.A., Hanson, R.K., Steeper R.R. and Fitzgerald, R.P.: Simultaneous imaging of exhaust gas residuals and temperature during HCCl combustion, Proc.Combust. Inst., 32, 2869−2876, 2009.

Singh, H. B., Thakur, A. N., Chen, Y.E. and Kanakidou, M.: Tetrachloroethylene as an indicator of low Cl atom in the troposphere, Geophys. Res. Lett., 23, 1529−1532, 1996.

Shimoda, M., Shigematsu, H., Shiratsuchi, H. and Osajima, Y.: Comparsion of volatile compounds among different grades of green tea and their relations to odor attributes. J. Agric. Food Chem. 43, 1621-1625. 1995.

Smith, A.A., Rigler, E., Kwok, E.S.C. and Atkinson, R.: Kinetics and products of the gas phase reactions of 6-methyl-5-hepten-2-one and trans-cinnamaldehyde with OH and NO_3 radicals and O_3 at 296±2K, Environ. Sci. Technol. 30, 1781-1785, 1996.

Spicer, C.W., Chapman, E. G., Finlayson-Pitts, B. J., Plastridge, R. A., Hubbe, J. M., Fast, J. D. and Berkowitz, C.M.: Unexpectedly high concentrations of molecular chlorine in coastal air. Nature, 394, 353−356, 1998.

Tanchotikul, U. and Hsieh, T.C.Y.: Volatile flavor components in crayfish waste, J. Food Sci., 54, 1515-1520, 1989.

Taatjes, C.A.: Time-resolved infrared absorption measurements of product formation in Cl atom reactions with alkenes and alkynes, Int.Rev.Phys.Chem. 18, 419-458, 1999.

Vijayakumar, S. and Rajakumar, B.: Kinetic investigation of chlorine atom initiated photo oxidation reactions of 2,3-dimethyl-1,3-butadiene in the gas phase: an experimental and theoretical study, RSC Adv., 6, 67739-67750, 2016.

Wang, K., Maofa, G. and Wang, W.: Kinetics of the gas phase reactions of 5-hexen-2-one with OH and NO_3 radicals and O_3, Chem. Phys. Lett. 490, 29-33, 2010.

Wiley-VCH, Ullmann's Encyclopedia of Industrial Chemistry, Seventh Ed., Werlag Gmbh: Weinheim, Germany, 2011.

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 N_2 relative to 1-pentene, 1,3-butadiene and isoprene.

Temperature (K)	Reference compound	$(k_{sample}/k_{reference})$ ±2σ	$(k_{sample}/k_{reference})_{Average}$ ±2σ	(k±2σ)×10^{-10}±2σ $cm^3molecule^{-1}s^{-1}$	(k±2σ)×10^{-10}±2σ $cm^3molecule^{-1}s^{-1}$	Literature (k±2σ)×10^{-10}±2σ ($cm^3molecule^{-1}s^{-1}$) at 298K
298±2	1,3-butadiene	1.55±0.21	1.46±0.36	5.08±0.36	5.54±0.41	3.00±0.58 [a]
		1.43±0.24				
		1.64±0.27				
		1.22±0.11				
	isoprene	1.63±0.15	1.61±0.03	5.84±0.03		
		1.62±0.11				
		1.60±0.13				
	1-pentene	1.12±0.12	1.21±0.26	5.71±0.26		
		1.09±0.13				
		1.33±0.10				
		1.33±0.10				

310±2	1-pentene	0.93±0.01	0.89±0.09	3.82±0.09	3.97±0.21	
		0.86±0.06				
	isoprene	1.24±0.10	1.29±0.07	4.13±0.07		
		1.37±0.10				
		1.26±0.09				
330±2	1-pentene	0.79±0.04	0.80±0.02	2.95±0.02	3.15±0.28	
		0.81±0.04				
	isoprene	1.24±0.10	1.15±0.07	3.36±0.07		
		1.13±0.09				
		1.09±0.08				
350±2	1-pentene	0.74±0.05	0.74±0.01	2.42±0.01	2. 63±0.29	
		0.75±0.06				
	isoprene	0.98±0.07	1.06±0.10	2.84±0.10		
		1.19±0.10				
		1.01±0.08				
363±2	isoprene	0.87±0.4	0.86±0.03	3.01±0.03	2.6±0.58	
		0.88±0.2				
		0.85±0.6				
	1-pentene	0.74±0.02	0.72±0.03	2.18±0.03		
		0.72±0.11				
		0.71±0.10				

[a] Blanco et al.

Table 2: Calculated total CVT/SCT rate coefficients (cm^3 molecule^{-1} s^{-1}) for the reaction of Cl atoms with 4-hexen-3-one obtained at the CCSD(T)/6-31+G(d,p)//MP2/6-311++G(d,p) level of theory.

Temperature (K)	**k (cm^3 molecule^{-1} s^{-1})**
275	5.81×10^{-10}
298	3.66×10^{-10}
325	2.33×10^{-10}
350	1.64×10^{-10}
375	1.22×10^{-10}
400	9.49×10^{-11}

Table 3: Barrier heights [$\Delta E^{0\ddagger}$, kcal mol^{-1}], kcal mol^{-1} at 298K], Gibbs free energy [ΔG^0 (298K), kcal mol^{-1}], heat of reaction [ΔH^0 (298K) and entropy of reaction [ΔS^0 (298K), cal mol^{-1} K^{-1}] for the reaction of Cl atoms with 4-hexen-3-one at the MP2/6-311++G(d, p) level of theory.

TSs	$\Delta E^{0\ddagger}$,kcal mol^{-1}	ΔH^0, kcal mol^{-1}	ΔG^0, kcal mol^{-1}	ΔS^0calmol^{-1} K^{-1}
TS1a	-3.80	-15.85	-7.81	-26.96
TS2a	-3.45	-16.35	-7.42	-29.94
TS1	10.63	2.21	-0.34	8.58
TS2	10.63	2.21	-0.34	8.58
TS3	11.36	2.21	-0.34	8.58
TS4	10.93	4.01	1.57	8.17
TS5	10.93	4.01	1.57	8.17
TS6	**17.97**	**15.88**	**13.82**	6.91
TS7	**17.97**	**21.86**	**19.73**	7.12
TS8	9.68	-3.04	-5.08	6.85
TS9	9.68	-3.04	-5.08	6.85
TS10	9.68	4.40	2.40	6.71

Table 4: Relative rate measurements for the reaction of Cl atoms with 5-hexen-2-one over the temperature range of 298-363K at 760 Torr in N_2 with reference to isoprene and 1-pentene.

T (K)	Reference compound	$(k_{sample}/k_{reference})\pm2\sigma$	$(k_{sample}/k_{reference})_{Average}\pm2\sigma$	$(k\pm2\sigma)\times10^{-10}$ ($cm^3molecule^{-1}s^{-1}$)	$(k_{Average}\pm2\sigma)\times10^{-10}$ ($cm^3molecule^{-1}s^{-1}$)	Lite.k×10^{-10} ($cm^3molecule^{-1}s^{-1}$) at 298K
298±2	1-pentene	0.87±0.09	0.91±0.08	4.27±0.08	4.00±0.37	3.15±0.5 [a]
		0.95±0.08				
		0.91±0.08				
	isoprene	1.18±0.09	1.09±0.11	3.74±0.11		
		1.14±0.1				
		0.97±0.16				
310±2	isoprene	1.06±0.08	1.09±0.09	3.51±0.09	3.77±0.35	
		1.13±0.06				
	1-pentene	0.94±0.08	0.94±0.08	4.04±0.08		
		0.95±0.09				
330±2	isoprene	1.05±0.06	1.07±0.05	3.11±0.05	3.11±0.01	
		1.09±0.08				
	1-pentene	0.84±0.06	0.84±0.01	3.12±0.01		
		0.85±0.09				
350±2	isoprene	1.17±0.16	1.14±0.07	3.07±0.07	3.00±0.55	
		1.12±0.13				
	1-pentene	0.92±0.10	0.91±0.02	2.94±0.02		
		0.89±0.09				
363±2	isoprene	0.98±0.07	1.05±0.11	2.67±0.11	2.66±0.03	
		0.99±0.09				
		1.18±0.08				
	1-pentene	0.89±0.05	0.88±0.02	2.65±0.02		

		0.88±0.07 0.87±0.06				

[a]Blanco et al.

Table 5: Barrier heights [$\Delta E^{0\ddagger}$, kcal mol^{-1} at 298K], heat of reaction [ΔH^0 (298K), kcal mol^{-1}], Gibbs free energy [ΔG^0 (298K), kcal mol^{-1}] and entropy of reaction [ΔS^0 (298K), cal mol^{-1} K^{-1}] for the reaction of Cl atoms with 5-hexen-2-one obtained at the MP2/6-311++G(d, p) level of theory.

TSs	$\Delta E^{0\ddagger}$, kcal mol^{-1}	ΔH^0, kcal mol^{-1}	ΔG^0, kcal mol^{-1}	ΔS^0calmol^{-1} K^{-1}
Ts1a	-3.63	-14.25	-6.39	-26.33
Ts2a	-3.68	-15.02	-6.34	-29.09
Ts1	15.83	6.42	5.13	5.81
Ts2	18.13	6.95	5.38	5.25
Ts3	14.49	6.28	4.95	5.08
Ts4	10.16	4.85	2.59	3.25
Ts5	9.56	4.26	2.47	3.86
Ts6	9.82	5.13	6.87	7.15
Ts7	7.30	4.95	6.51	5.25
Ts8	**15.8**	**11.56**	**8.56**	6.19
Ts9	**18.06**	**12.45**	**9.47**	7.48
Ts10	**20.42**	**12.35**	**9.66**	5.66

Table 6: Calculated total CVT/SCT rate coefficients (cm^3 molecule^{-1} s^{-1}) for the reaction of Cl atoms with 5-hexen-2-one obtained at CCSD(T)/6-31+G(d,p)//MP2/6-311++G (d, p) level of theory.

Temperature(K)	**k (cm^3 molecule^{-1} s^{-1})**
275	1.09×10^{-09}
298	5.56×10^{-10}
325	3.85×10^{-10}
350	2.44×10^{-10}
375	1.57×10^{-10}
400	1.00×10^{-10}

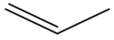
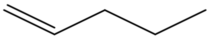
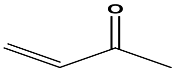
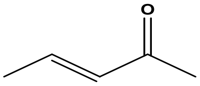
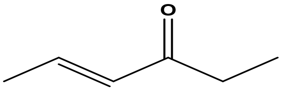
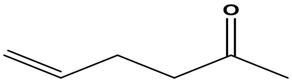
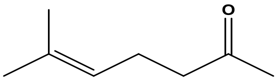
Table 7: Calculated total CVT/SCT rate coefficients (cm^3 molecule^{-1} s^{-1}) for the reaction of Cl atoms with 3-penten-2-one obtained at the CCSD(T)/6-31+G(d, p)//MP2/6-311++G (d, p) level of theory.

Temperature(K)	**k (cm^3 molecule^{-1} s^{-1})**
275	3.51×10^{-10}
298	2.40×10^{-10}
325	1.66×10^{-10}
350	1.26×10^{-10}
375	9.89×10^{-11}
400	8.07×10^{-11}

Table 8: Barrier heights [$\Delta E^{0\ddagger}$, kcal mol^{-1} at 298K], heat of reaction [ΔH^0 (298K), kcal mol^{-1}], Gibbs free energy [ΔG^0 (298K), kcal mol^{-1}] and entropy of reaction [ΔS^0 (298K), cal mol^{-1} K^{-1}] for the reaction of Cl atoms with 3-penten-2-one at the MP2/6-311++G (d, p) level of theory.

TSs	$\Delta E^{0\ddagger}$,kcal mol^{-1}	ΔH^0, kcal mol^{-1}	ΔG^0, kcal mol^{-1}	ΔS^0calmol^{-1}K^{-1}
Ts1a	-4.12	-15.23	-7.57	-25.70
Ts2a	-3.75	-15.57	-6.97	-28.85
Ts1	13.94	4.32	3.13	6.81
Ts2	14.23	4.15	3.09	6.24
Ts3	14.23	4.15	3.09	6.24
Ts4	**15.85**	**14.89**	**11.57**	8.23
Ts5	**19.45**	**14.25**	**11.62**	8.48
Ts6	9.82	2.38	4.25	5.87
Ts7	10.17	2.61	4.60	6.69
Ts8	10.17	2.61	4.60	6.69

Table 9: Reactivity of series of unsaturated ketones with Cl atoms, OH and NO_3 radicals at 298K.

Molecule	k_{Cl} **(cm^3 molecule^{-1} s^{-1})**	k_{OH} **(cm^3 molecule^{-1} s^{-1})**	k_{NO3} **(cm^3 molecule^{-1} s^{-1})**
 **propene**	2.7×10^{-10} [a]	2.63×10^{-11} [d]	9.5×10^{-15} [d]
 **1-pentene**	4.0×10^{-10} [a]	3.14×10^{-11} [d]	1.51×10^{-14} [d]
 **3-buten-2-one**	0.99×10^{-10} [b]	1.86×10^{-11} [d]	5.47×10^{-16} [d]
 **3-penten-2-one**	2.40×10^{-10} [c]	7.22×10^{-11} [e]	1.03×10^{-14} [e]
 **4-hexen-3-one**	3.66×10^{-10} [c]	9.04×10^{-11} [e]	0.63×10^{-14} [e]
 **5-hexen-2-one**	5.56×10^{-10} [c]	5.18×10^{-11} [e]	2.16×10^{-14} [e]
 **6-methyl-5-hepten-2-one**	-	1.57×10^{-10} [a]	7.5×10^{-12} [a]

[a] Smith et al., [b] Canosa-Mas et al., [c] Present work, [d] Atkinson et al., [e] Wang et al.

Table 10: Atmospheric lifetimes (τ) calculated for series of unsaturated ketones with different atmospheric oxidizing agents at 298K.

	Cl atoms[a]		OH radicals [b]		NO_3 radicals [c]		O_3 radicals[c]		Cumulative life times
Molecule	**k_{Cl} ×10^{10}**	**τ (hr)**	**k_{OH} ×10^{11}**	**τ (hr)**	**k_{NO3} ×10^{14}**	**τ (hr)**	**k_{O3} ×10^{17}**	**τ (hr)**	**$τ_{eff}$ (hr)**
4-hexen-3-one	3.66	3.5	9.04	2	0.63	87	6.37	6	1.04
5-hexen-2-one	5.56	5.3	5.18	3	2.16	26	0.91	43	1.75
3-penten-2-one	2.40	8.7	7.22	2	1.03	54	2.95	13	1.41

[a]present work, [b]Blanco et al., [c]Wang et al.

Table 11: Branching ratios for the reactions of Cl atoms with 4-hexen-3-one, 5-hexen-2-one and 3-penten-2-one.

	4-hexen-3one			**5-hexen-2-one**			**3-penten-2-one**		
T (K)	TS1a	TS2a	Total abstraction	TS1a	TS2a	Total abstraction	TS1a	TS2a	Total abstraction
200	68.70	31.21	0.10	55.70	44.27	0.02	66.37	33.62	0.01
225	66.65	33.12	0.24	56.31	43.62	0.07	64.62	35.36	0.02
250	64.85	34.68	0.48	56.71	43.13	0.16	63.18	36.76	0.06
275	63.20	35.97	0.83	56.93	42.77	0.30	61.96	37.91	0.13
298	61.92	36.99	1.10	56.97	42.52	0.52	60.96	38.81	0.23
325	60.64	38.01	1.35	56.91	42.30	0.79	59.92	39.71	0.38
350	59.50	38.83	1.67	56.73	42.15	1.12	59.01	40.42	0.56
375	58.52	39.56	1.92	56.46	42.04	1.49	58.16	41.05	0.79
400	57.71	40.20	2.09	56.13	41.97	1.90	57.35	41.61	1.04

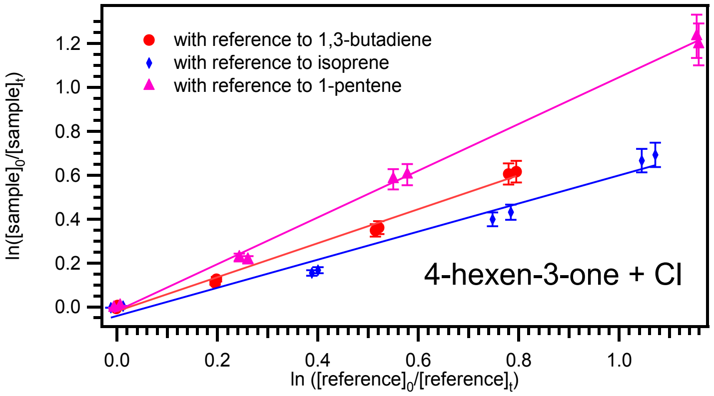


Figure 1: Plot of the relative decrease in the concentration of 4-hexen-3-one due to its reaction with Cl atoms relative to 1-pentene, 1,3-butadiene and isoprene at 298K.

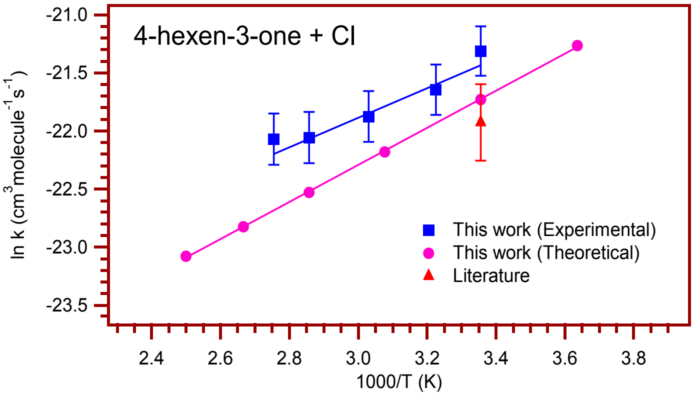
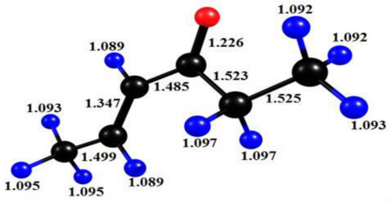
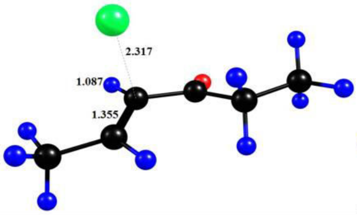


Figure 2: Arrhenius plot of CVT/SCT rate coefficients calculated at the CCSD(T)/6-31+G(d, p)//MP2/6-311++G(d,p) level of theory between the temperatures 275 and 400 K and experimentally measured rate coefficients between the temperatures of 298 and 363 K for the reaction of Cl atoms with 4-hexen-3-one.

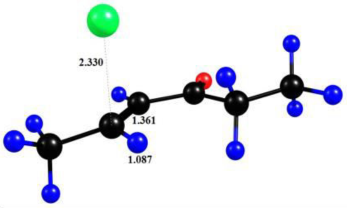
Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-163, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 12 April 2017



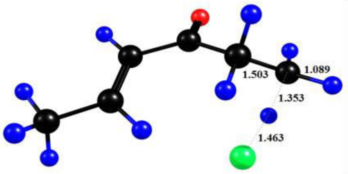
4-hexen-3-one



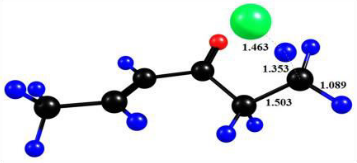
TS1a



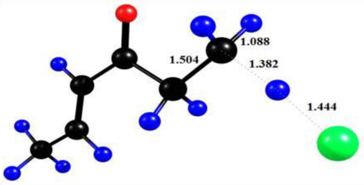
TS2a



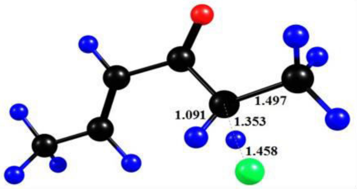
TS1



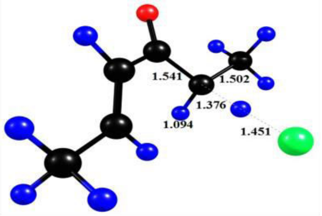
TS2



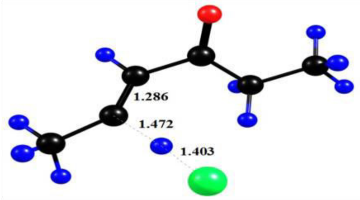
TS3



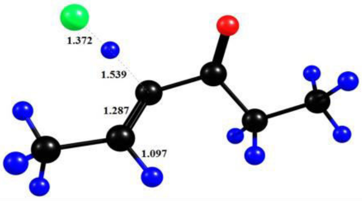
TS4



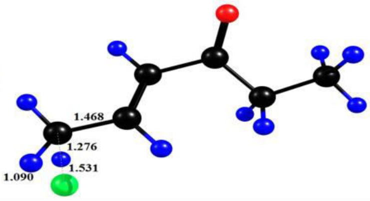
TS5



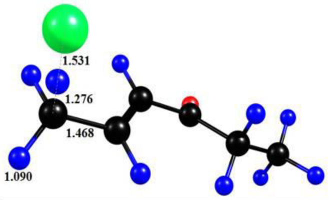
TS6



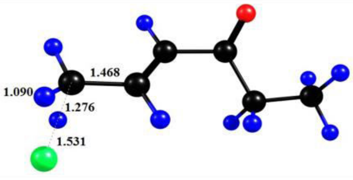
TS7



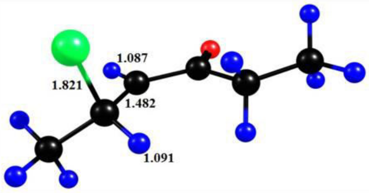
TS8



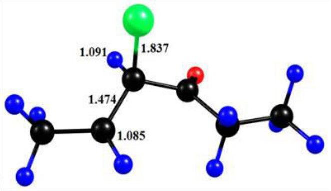
TS9



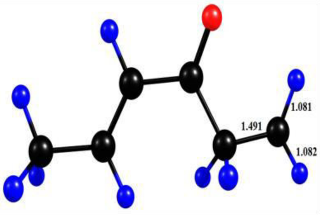
TS10



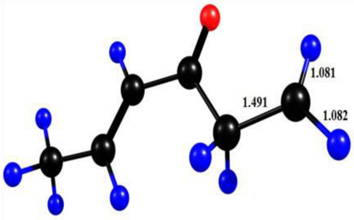
P1a



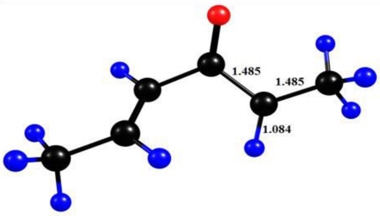
P2a



P1, P2



P3



P4, P5

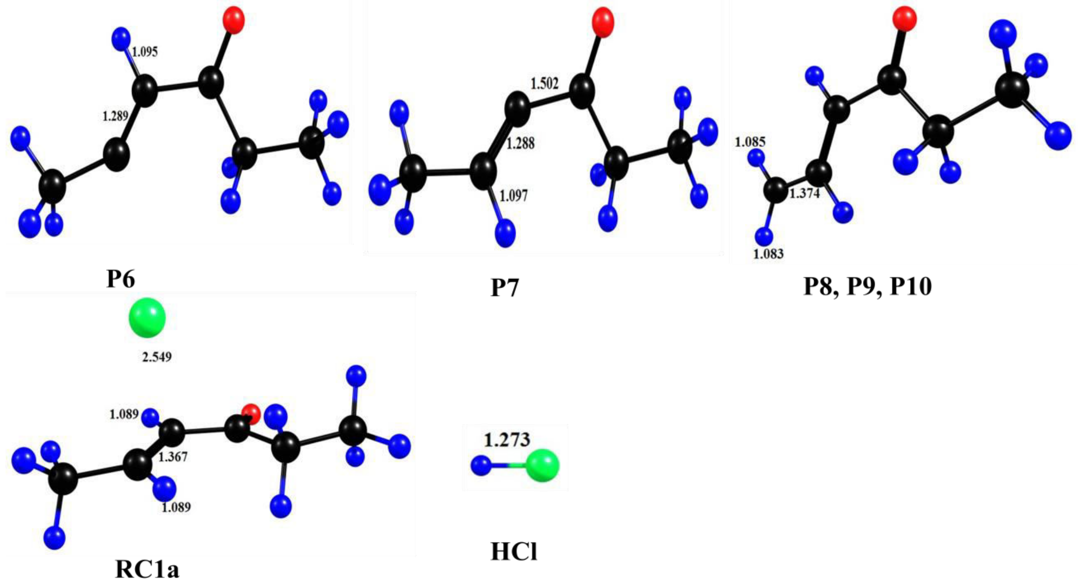


Figure 3: Optimized geometries of the reactants, pre-reactive complexes, transition states and products for the reaction of Cl atoms with 4-hexen-3-one obtained at MP2/6-311++G(d,p) level of theory. Black color represents carbon atoms, blue color represents hydrogen atoms, red color represents oxygen atoms and green color represents Cl atoms.

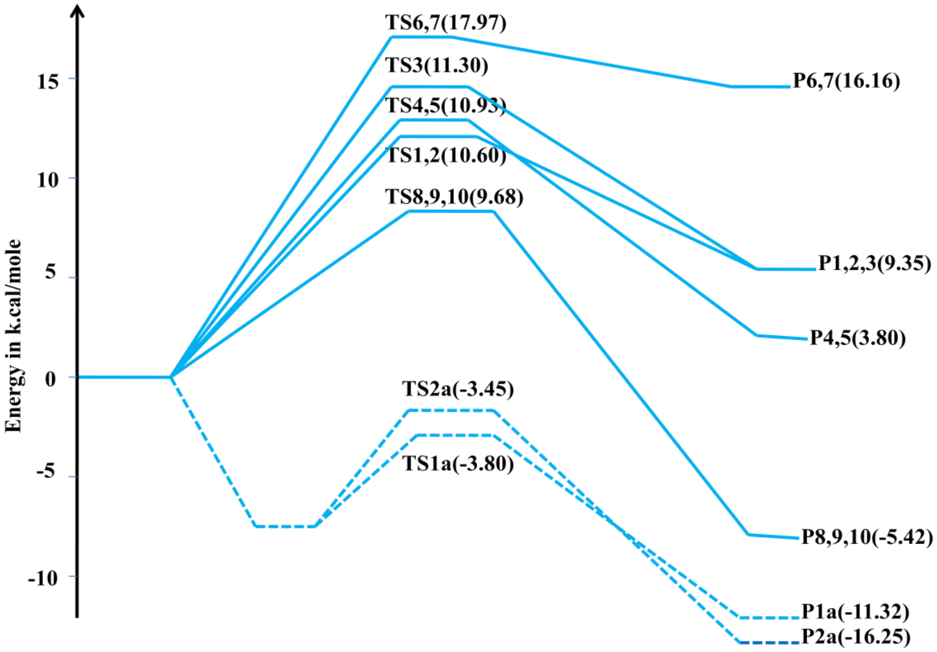


Figure 4: Potential energy diagram for the reaction of Cl atoms with 4-hexen-3-one obtained at CCSD(T)/6-31+G(d,p)//MP2/6-311++G(d,p) level of theory at 298K.

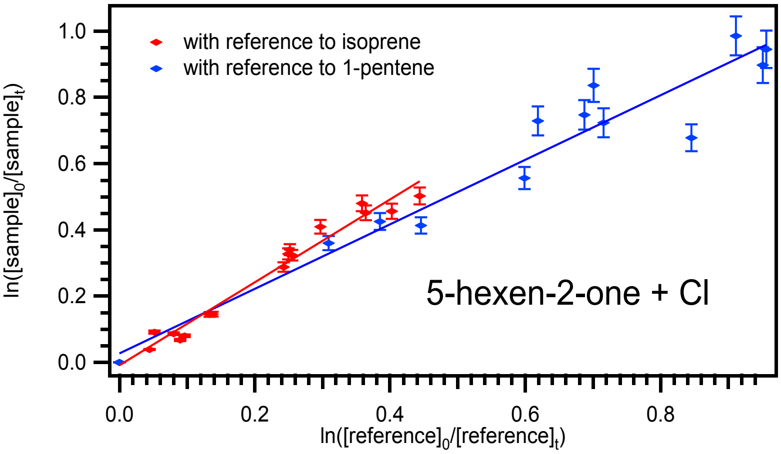


Figure 5: Plot of the relative decrease in the concentration of 5-hexen-2-one due to its reaction with Cl atoms relative to isoprene and 1-pentene at 298K.

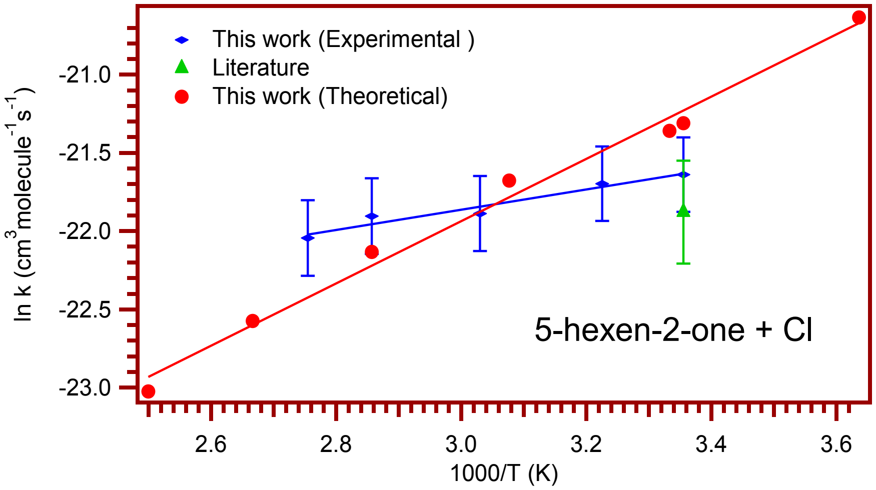
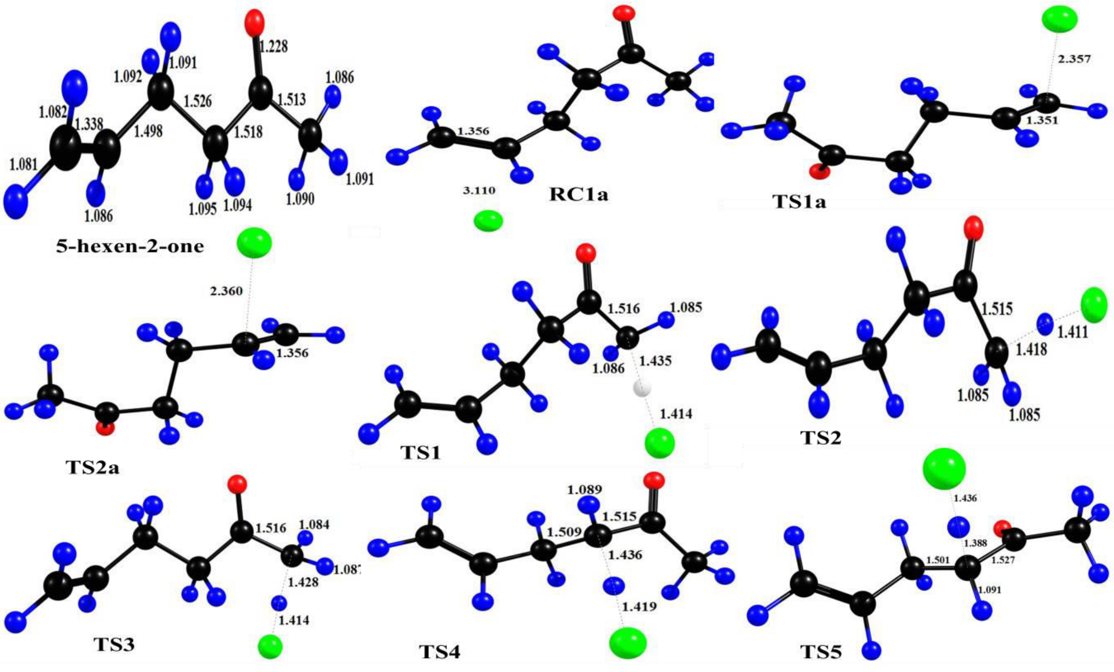


Figure 6: Arrhenius plot of CVT/SCT rate coefficients obtained at the CCSD(T)/6-31+G(d, p)//MP2/6-311++G(d,p) level of theory between the temperatures 275 and 400 K and experimentally measured rate coefficients between the temperatures of 298 and 363 K for the reaction of Cl atoms with 5-hexen-2-one.



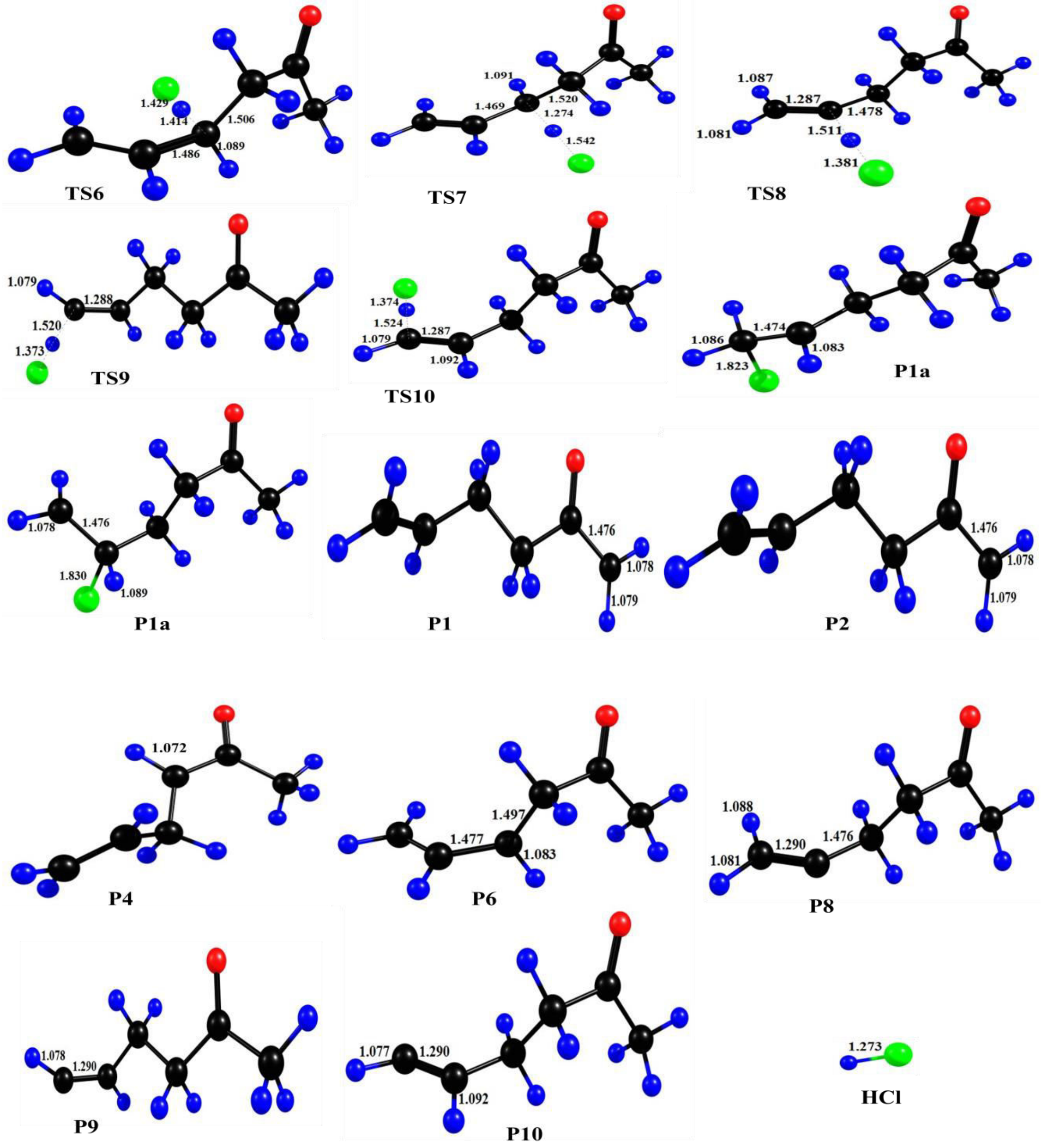


Figure 7: Optimized geometries of the reactants, pre-reactive complexes, transition states and products for the reaction of Cl atoms with 5-hexen-2-one obtained at MP2/6-311++G(d, p) level of theory. Black color represents carbon atoms, blue color represents hydrogen atoms, red color represents oxygen and green color represents Cl atoms.

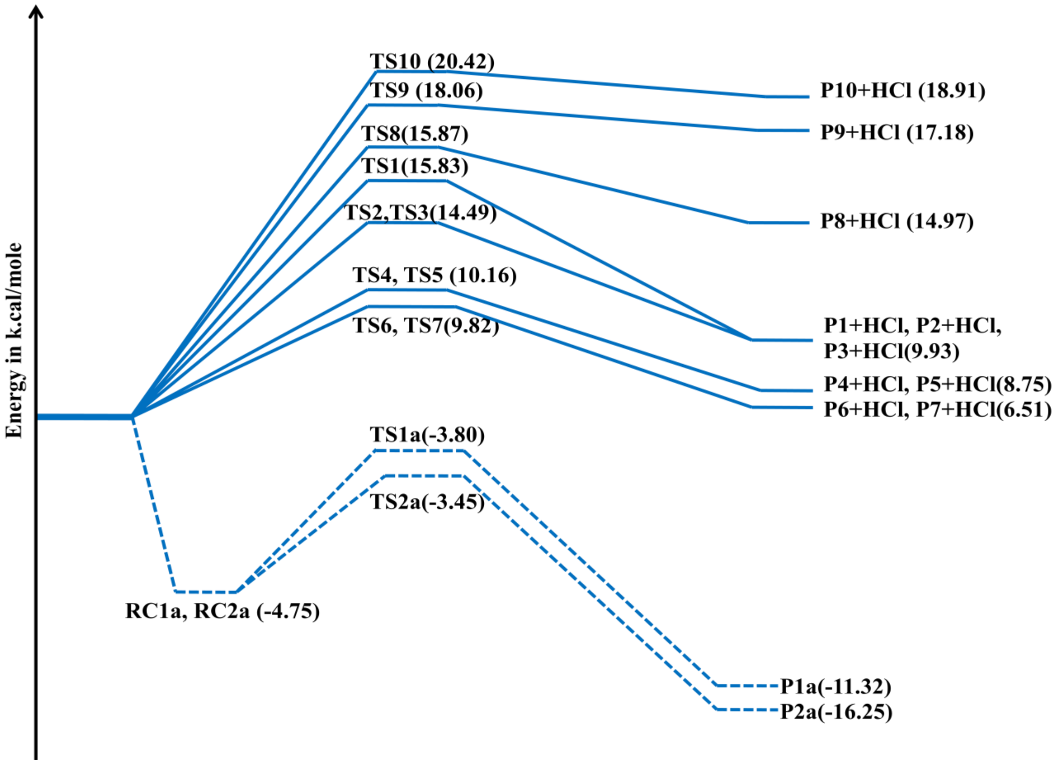
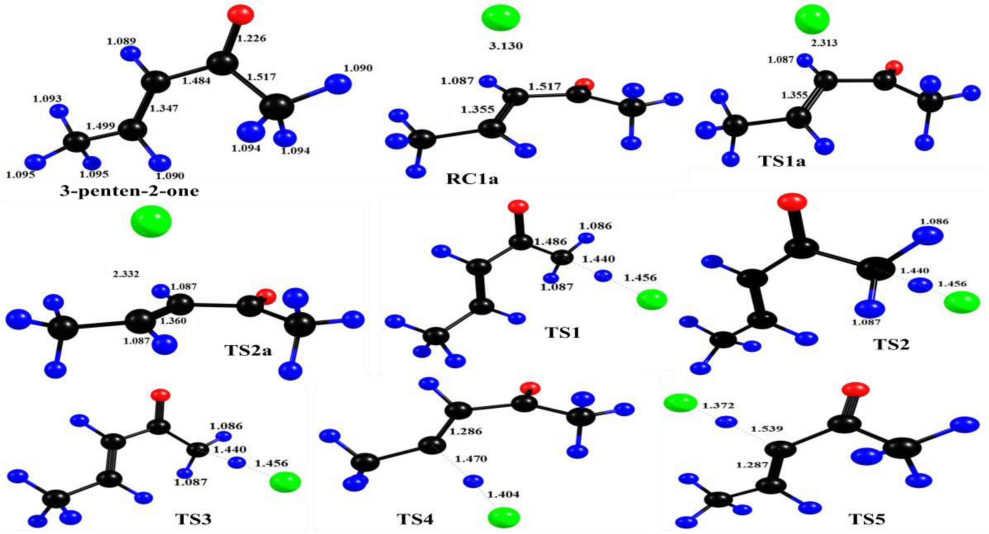


Figure 8: Potential energy diagram for the reaction of Cl atoms with 5-hexen-2-one obtained at CCSD(T)/6-31+G(d,p)// MP2/6-311++G(d, p) level of theory at 298K.



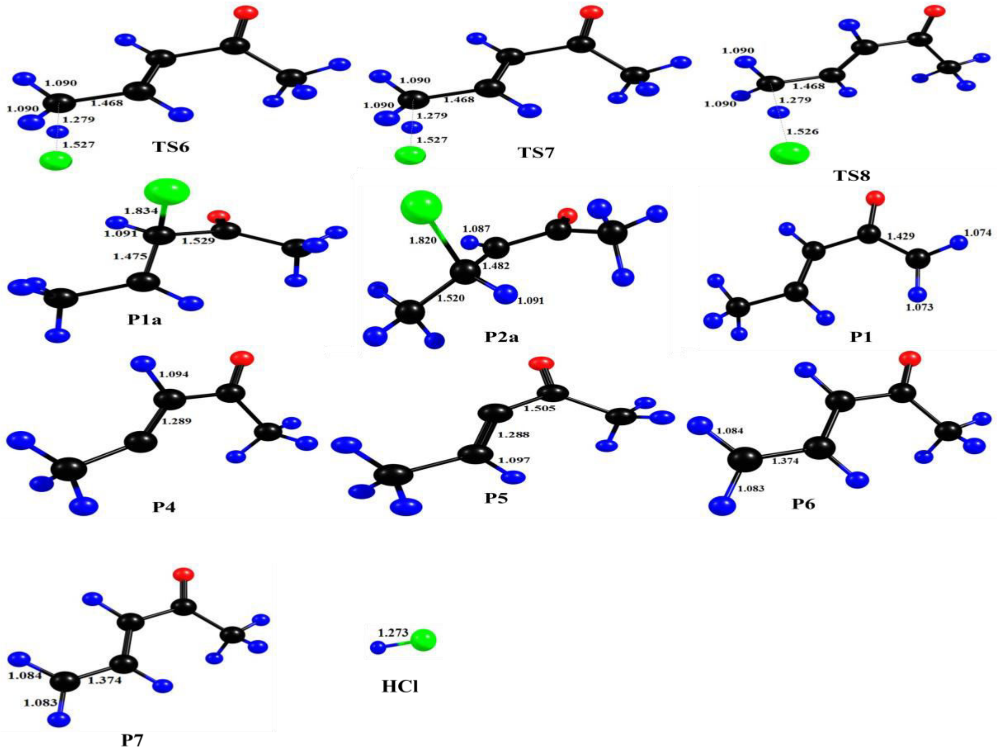


Figure 9: Optimized geometries of the reactants, pre-reactive complexes, transition states and products obtained MP2/6-311++G(d,p) level of theory. Black color represents carbon atoms, blue color represents hydrogen atoms, red color represents oxygen and green color represents Cl atoms.

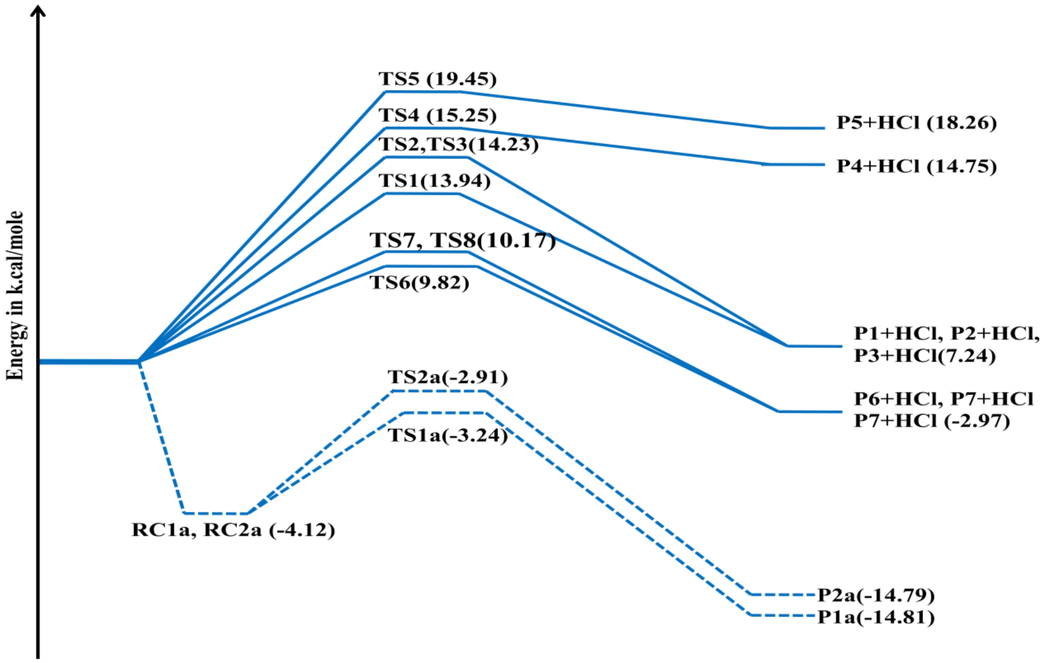


Figure 10: Potential energy diagram for the reaction of Cl atoms with 3-penten-2-one obtained at CCSD(T)/6-31+G(d, p)// MP2/6-311++G(d, p) level of theory at 298K.

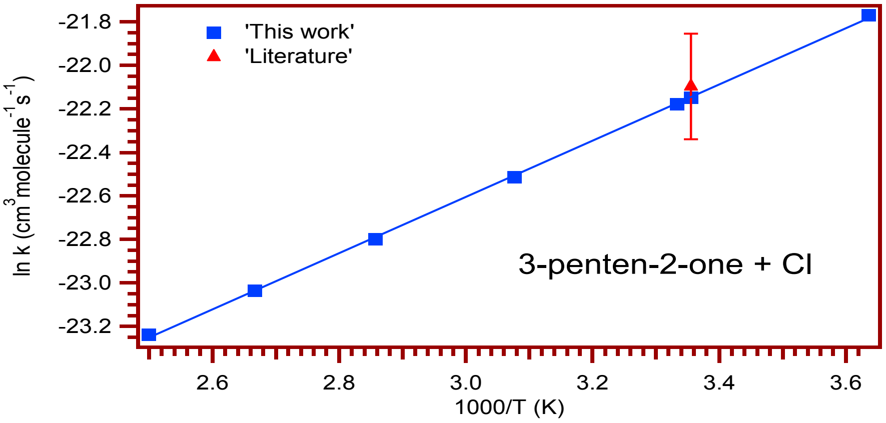


Figure 11: Arrhenius plot of CVT/SCT rate coefficients obtained at the CCSD(T)/6-31+G(d, p)// MP2/6-311++G(d,p) level of theory between the temperatures 275 and 400 K for the reaction of Cl atoms with 3-penten-2-one.

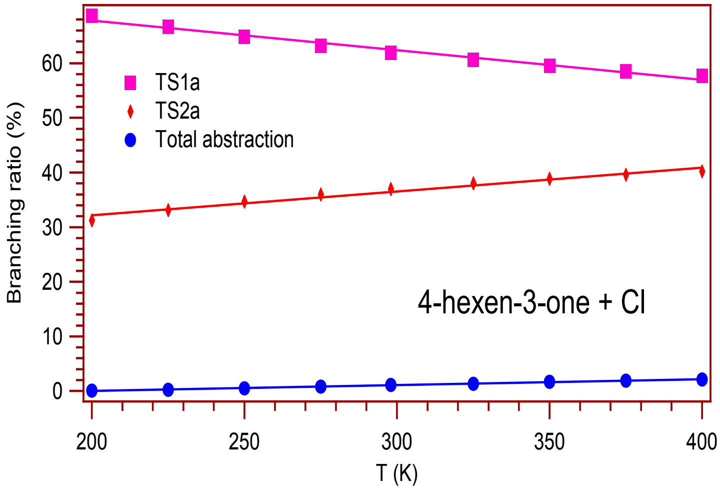


Figure 12: Calculated branching ratios vs temperature for the reaction of Cl atoms with 4-hexen-3-one.

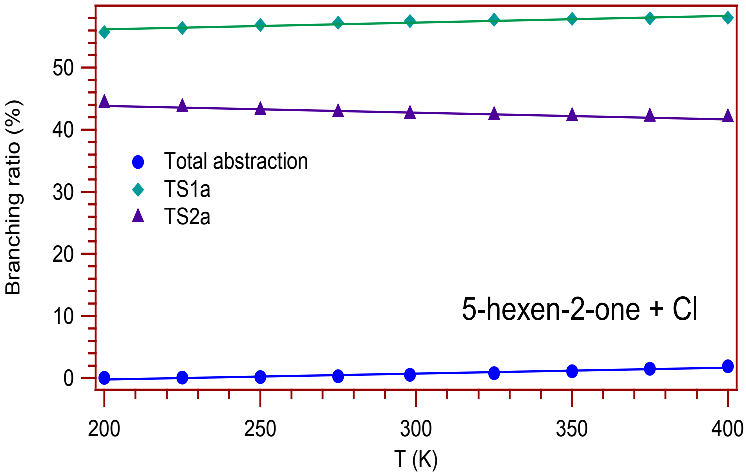


Figure 13: Calculated branching ratios vs temperature for the reaction of Cl atoms with 5-hexen-2-one.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-163, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 12 April 2017

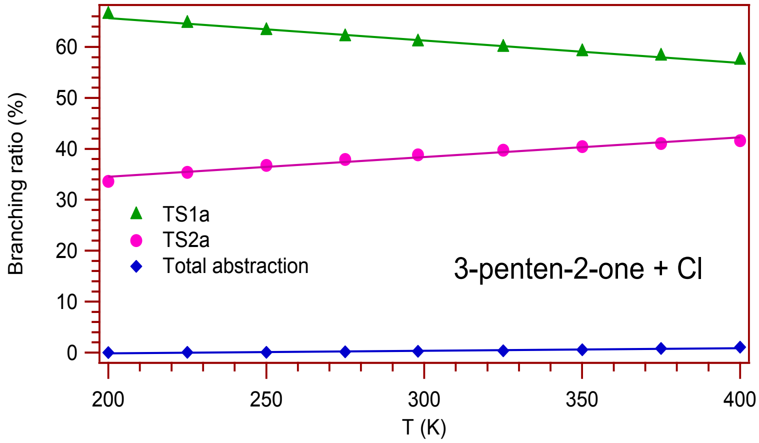
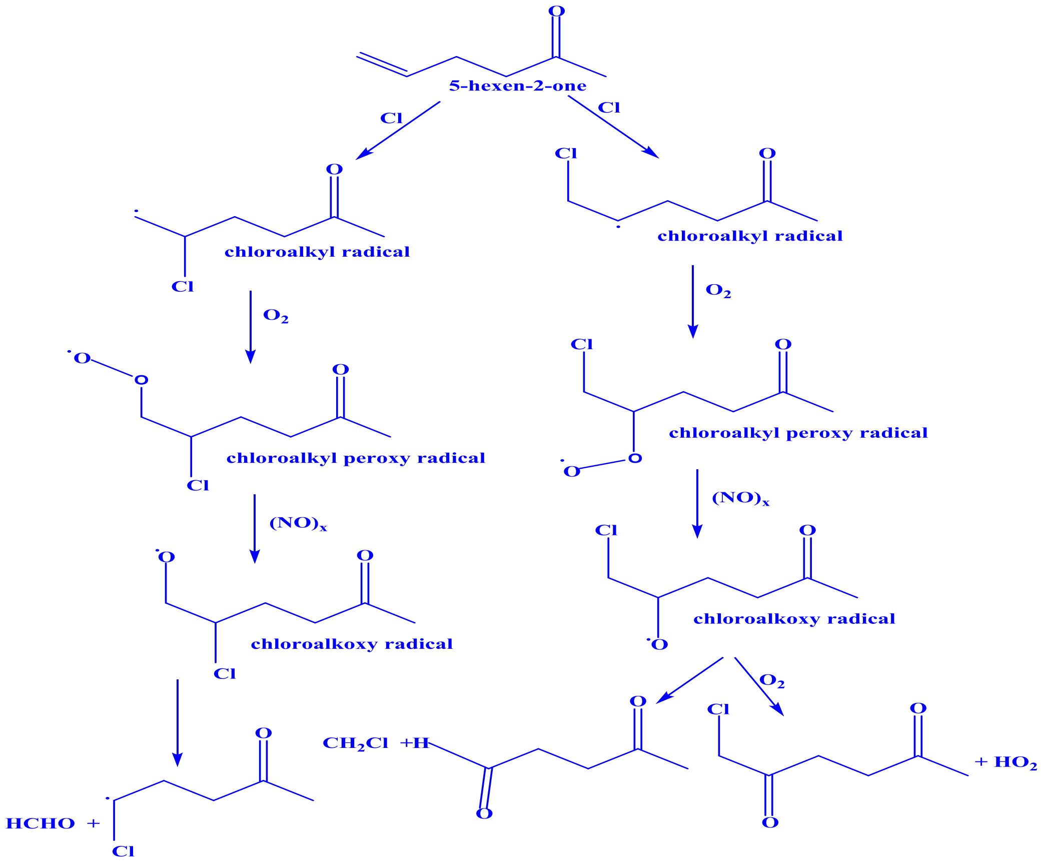


Figure 14: Calculated branching ratios vs temperature for the reaction of Cl atoms with 3-penten-2-one.



1

2

3 **Figure 15:** Atmospheric degradation mechanism for the reaction of Cl atom with 5-hexen-2-one.

4