Is H Atom Abstraction Important in the Reaction of CI with 1-Alkenes?

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Supporting Information

ABSTRACT: The relative yields of products of the reaction of Cl atoms with 1-alkenes (C4–C9) were determined to see whether H atom abstraction is an important channel and if it is to identify the preferred position of abstraction. The presence of all the possible positional isomers of long chain alkenones and alkenols among the products, along with chloroketones and chloroalcohols, confirms the occurrence of H atom abstraction. A consistent pattern of distribution of abstraction products is observed with oxidation at C4 (next to allyl) being the lowest and that at CH_2 groups away from the double bond being the highest. This contradicts with the higher stability of allyl (C3) radical. For a better understanding of the relative reactivity, ab initio calculations at MP2/6-311+G (d,p) level of theory are carried out in the case of 1-heptene. The total rate coefficient, calculated using conventional transition state theory, was found to be in good agreement with the experimental value at room



temperature. The preferred position of Cl atom addition is predicted to be the terminal carbon atom, which matches with the experimental observation, whereas the rate coefficients calculated for individual channels of H atom abstraction do not explain the observed pattern of products. The distribution of abstraction products except at C4 is found to be better explained by reported structure activity relationship, developed from experimental rate coefficient data. This implies the reactions to be kinetically dictated and emphasizes the importance of secondary reactions.

1. INTRODUCTION

It is well established that Cl atom initiated oxidation of volatile organic compounds (VOCs) contribute significantly to the generation of ozone and organic aerosols in the coastal areas and marine boundary layer.^{1,2} Many recent studies have emphasized the significant role of Cl atom as an oxidant in the polluted urban atmosphere.³ Among the various VOCs, unsaturated hydrocarbons play an important role in the tropospheric chemistry.^{4,5} Among them, long chain 1-alkenes, such as 1-hexene have been detected in the marine boundary layer⁶ and also higher alkenes up to 1-decene have been detected in the polluted urban air.⁷ There were some studies on the reactions of these higher alkenes with $OH_{,8}^{8} O_{3,9}^{9,10}$ and $NO_{3,9}^{11,12}$ which are the major tropospheric oxidants.¹³ The significant concentration of Cl atoms available in the coastal conditions^{3,14–16} emphasizes the importance of the reactions of these alkenes with Cl atom. However, the rate coefficients and major products of the reactions of Cl atoms with long chain 1alkenes (C6–C9) are reported only recently.¹⁷ This study confirmed that the reaction of 1-alkenes with Cl atom is equally important as that of OH in initiating degradation of 1-alkenes, in the conditions of marine boundary layer.

Reaction of Cl atom resembles that of OH radical with respect to the mechanism, the reaction pathways being addition to the double bond and abstraction of H atoms from the alkyl groups. However, there is a significant difference in the rate coefficients of the reactions, being more than an order of magnitude higher for Cl reactions, especially in the case of saturated hydrocarbons, where only abstraction reaction takes place. Ezell et al.¹⁸ estimated the rate coefficient of addition to be about $2.6-2.7 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ for 1-alkenes and the abstraction rate coefficients at allyl groups were estimated to be $3.4-4.5 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, based on the fitting of the available data. The surprising result that they mentioned was that the rate coefficients of abstraction of allylic hydrogen atoms are smaller than the expected values. This contradicts with the significant yields of products formed by H abstraction from allyl carbon atoms during the reaction of Cl with propene and isoprene.^{19,20} The dependence on pressure suggested the possibility of addition-elimination reaction at allyl position in addition to direct abstraction by Cl atom.¹⁹ In the case of cyclic alkenes and dienes, the estimated rate coefficients of H atom abstraction by Cl atom were found to be similar for allylic and nonallylic positions.²¹ Our recent study on the rate coefficients of Cl atom reactions of 1-alkenes showed H abstraction from allyl as well as nonallyl positions to be occurring as minor pathways, along with the major channel of Cl addition reaction.¹⁷ Although all the results emphasize the importance

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of abstraction channels in reactions of Cl with long alkenes, detailed product analysis to determine the relative contribution of abstraction from different carbon atoms from C3 to the terminal CH_3 groups is not carried out so far. In view of the contradicting observations mentioned above, ¹⁸⁻²⁰ it is important to know the significance of abstraction from the C3 position leading to allyl radical and that of addition reactions. Further reactions of these primary radical products are also important in assessing the overall environmental impact. Occurrence of abstraction is also identified during the reaction of the long chain 1-alkenes with OH radicals.^{8,22,23} However, the complexity due to isomerization of the intermediate alkoxy radicals and the formation of multifunctional products arising from the addition of OH and abstraction channels, and very low yield of abstraction products make it difficult to identify and quantify the individual products. Because the product radical of abstraction reaction is the same in OH and Cl reactions, a study on the products of Cl atom reactions, having more probability of abstraction due to higher rate coefficients, is expected to lead to a better understanding on the secondary chemistry of these radicals. In our previous study,¹⁷ some of the products were identified but quantitative comparison could be carried out only for smaller aldehydes. The present study focuses more on the isomers of long chain products of abstraction and addition reactions, using both mass spectroscopy (MS) and flame ionization detection (FID).

Although the relative importance of abstraction can be understood from the rate coefficients of individual primary reactions of addition and abstraction from different positions, these are not known and cannot be deducted from the products due to the complex secondary chemistry. However, theoretical methods based on MP2 theory with TST/VTST calculations have been successful in calculating rate coefficients, which agree well with the experimental ones.²⁴ This information is useful in understanding the relative importance of different channels of the reactions in many cases, even when absolute values deviate from the experimental ones. Thus, the theoretically estimated rate coefficients of different channels of reactions of Cl with 1alkenes and the comparison of the expected product distribution with the observed one can probably give an insight into the major secondary reactions of these radicals. Although potential energy surface of reaction of Cl with 1-propene has been studied recently,²⁵ the computational methods are being applied to the kinetics of reactions of Cl with long chain 1alkenes for the first time. Detailed theoretical study is carried out in a typical case, 1-heptene, and the results are compared with the experimentally observed product distribution.

2. EXPERIMENTAL SECTION

All the experiments were performed at 298 ± 2 K. The details of the experimental setup are given elsewhere.²⁶ The reaction mixture, consisting of alkenes (200–250 ppm), CCl₃COCl, the source molecule for Cl atom (500–600 ppm), and buffer gas (N₂/air), was photolyzed in a quartz reactor cells of volume of about 1 and 3 L. The cell is provided with a sealed port for taking out samples for concentration measurements. The total pressure was maintained at 800 \pm 3 Torr. Photolysis of CCl₃COCl at 254 nm generates the Cl atom. The mixture was photolyzed for a period of 6 min in steps of 2–3 min each, and the total depletion of the parent alkene was maintained around 35 \pm 5%. The products were separated and identified by gas chromatograph coupled with a mass spectrometer (GCMS- QP2010, Shimadzu). FID was employed for monitoring the depletion in the alkene quantitatively and to estimate the relative yields of the products. Three different columns, namely CP-wax, Q-Plot and HT8, were used for separation.

Ultrapure air (Zero grade; Chemtron Science Laboratories, India) was used as the buffer gas. 1-Hexene (99%), 1-heptene (97%), 1-octene (98%), and 1-nonene (96%) from Sigma-Aldrich and *n*-butane and 1-butene from Matheson were used without further purification. Samples of the compounds were stored in evacuated glass vessels and subjected to freeze– pump-thaw cycles prior to use.

2.1. Computational Methods. Ab initio calculations were performed to calculate the rate coefficients for the reaction of chlorine atoms with 1-heptene. The geometries of the reactant (1-heptene), transition states of addition and abstraction channels (TSs), all the products, prereactive complexes (RCs), and product complexes (PCs) were optimized at Møller-Plesset²⁷ second order (MP2) theory including all electrons in correlation with the Pople's basis set 6-311+G-(d,p). All the normal modes of vibrations and structures were viewed in Gauss view.²⁸ Transition states (TSs) were confirmed with one imaginary frequency, reactants and products were identified with zero imaginary frequencies. Intrinsic reaction coordinate²⁹ (IRCs) calculations were carried out using MP2/ 6-311+G (d,p) level of theory to verify that all the transition states were connected to the reactants and products. Structural parameters obtained at MP2 level of theory and Gaussian 09 program suite³⁰ were used in all the kinetic calculations.

Kinetics. Rate coefficients for the addition and abstraction reactions of 1-heptene with Cl atoms were computed using conventional transition state theory $(\text{CTST})^{31}$ in conjugation with MP2/6-311+G(d,p) level of theory over the temperature range of 200–400 K.

$$k(T) = l \frac{k_{\rm B}T}{h} \left(\frac{Q_{\ddagger}}{Q_{\rm R}} \right) \exp \left(-\frac{\Delta E_0}{RT} \right)$$

where *l* is the reaction path degeneracy, $k_{\rm B}$ is the Boltzmann constant, and *h* is Planck's constant. *T* is temperature in Kelvin, Q_{\ddagger} and $Q_{\rm R}$ are the partition functions of the TS and reactant, respectively. ΔE_0 is the molar zero-point energy inclusive barrier height, and *R* is the universal gas constant. The electronic partition function³² of the chlorine atom was evaluated by taking the splitting of 881 cm⁻¹ between the ground state ${}^2\mathrm{P}_{3/2}$ and excited state ${}^2\mathrm{P}_{1/2}$ into account.

3. RESULTS

3.1. Distribution of Products. Figure 1 shows the products in the typical case, reaction of Cl with 1-heptene, detected using flame ionization detectors and identified using mass spectrometry. Photolysis duration was varied to vary the extent of photolysis of CCl₃COCl, thereby varying the percentage of alkene that has reacted, and the product distribution was found to be the same in all cases. The details, including the extent of reaction, are summarized in Table 1. The results shown are from four independent experiments, each value being the average of at least 3-4 chromatograms. The major products are 1-chloro-2-heptanone and 1-chloro-2heptanol (Group D) along with smaller yields of enols (Group C), enones (Group B), and smaller aldehydes, such as propenal, propanal and butanal (Group A). The retention times with FID and MS are almost the same under the same column conditions, the minor difference being mainly due to



Figure 1. Chromatogram showing the products of reaction of Cl with 1-heptene. Inset: The mass spectra of the four alkenones, shown as group B. B1, 1-hepten-4-one, B2, 1-hepten-3-one, B3, 6-hepten-3-one (1-hepten-5-one), B4, 6-hepten-2-one (1-hepten-6-one).

the difference in the carrier gas.¹⁷ The products were identified by direct matching carried out by the instrument software wherever the data are available in the standard libraries or by studying their fragmentation pattern for molecules without prior data. The experiments in reactors of 3 and 1 L yielded the same product distribution pattern.

The product distributions observed in 1-hexene, 1-octene, and 1-nonene are very similar to that described above for 1-heptene with chlorosubstituted ketones and alcohols formed by addition at the double bond as the major products. It is also to be noted that no other Cl containing fragment was identified in the case of 1-hexene, 1-heptene, 1-octene, and 1-nonene, unlike the case of 1-butene where chloroacetaldehyde was identified as one of the major products in addition to chlorobutanone and chlorobutanol.¹⁷

The number of isomers of enones and enols are found to be increasing with the number of carbon atoms with products corresponding to oxidation at all the possible positions but with different yields, as shown in Figure 2 for enones. In the absence of standards, a quantitative comparison of the yields is possible Article

by comparing the areas, which in turn depend on the response of the FID. The FID relative response factors can be correlated to the effective carbon numbers (ECN) of the products,³³ which depend on the functional groups present, and contribution of common functional groups to the ECN of a compound have been experimentally determined.³³ In the present case of alkenones, where the number of carbon atoms and functional groups are the same, the ECN and hence the FID response is expected to be equal, and the areas in chromatograms can be directly compared for relative concentration. The relative yields are obtained based on the areas under the peaks, as shown in Table 2. As in the case of 1heptene, at least three to four independent experiments were carried out for each alkene, keeping the depletion almost 35 \pm 5%, the chromatograms were recorded 3-4 times for each experiment, and the average ratios are given. The product distribution pattern, that is, the ratios of different positional isomers of alkenones, was found to be consistent in all cases. The yield of alkenone with keto group at carbon atoms next to allyl carbon, that is, at fourth carbon atom, is the lowest in all cases. Although the ECN for ketone is expected to be lower than that of the corresponding alcohol,³³ the areas of the enols are lower than that of enones, indicating a lower yield. The absence of a prominent peak corresponding to 6-hepten-4-ol among the products of 1-heptene is consistent with the low yield of the corresponding enone, suggesting the mechanism of formation of alcohol and enone to be similar. Along with the enols, the terminal unsaturated aldehyde is also observed but with lower yield. Among the smaller aldehydes, the dominance of those with 3 carbon atoms lower than that of parent alkene, that is, propanal in 1-hexene, butanal in 1-heptene, pentanal in 1-octene, and hexanal in 1-nonene, has already been noted.¹⁷ Propenal is observed in all these cases. In the case of addition products, the areas of chloroketones are always more than two times that of the corresponding chloroalcohols, very similar to the dominance of ketones in the abstraction reaction products. The ion chromatograms, recorded by GC-MS, also show larger area for chloroketones as compared to the corresponding alcohols, confirming this to be not due to difference in the sensitivity of keto and alcohol functional groups.

Table 1. Details of the Products of Cl Initiated Oxidation of 1-Heptene, Observed by GC-FID

heptene	retention time	I	II	III	IV	average
area of 1-heptene before photolysis		2.78×10^{6}	2.73×10^{6}	2.91×10^{6}	3.07×10^{6}	2.87×10^{6}
area after photolysis		1.67×10^{6}	1.70×10^{6}	1.84×10^{6}	2.02×10^{6}	1.80×10^{6}
% depletion		39.9	37.7	36.8	34.2	37.2
propanal	2.21 min	3703	3364	3649	3299	3504
propenal	2.67 min	2678	2677	2762	2515	2658
butanal	2.95 min	7224	6863	7237	6648	6993
pentanal	4.91 min	1231	1502	1647	1308	1422
hexanal	8.19 min	1841	1882	1706	1684	1778
1-hepten-4-one (at C4)	12.02 min	1475	1633	1781	1607	1624
1-hepten-3-one (at C3)	12.28 min	4191	4290	5002	4568	4513
6-hepten-3-one (at C5)	12.37 min	7941	8474	9604	8515	8634
6-hepten-2-one (at C6)	13.16 min	7619	8333	9352	8174	8370
1-heptenal	16.28 min	1959	2374	2667	2194	2299
6-hepten-3-ol	17.10 min	1438	1576	1769	1898	1670
1-hepten-3-ol	17.32 min	1191	1430	1727	1502	1463
6-hepten-2-ol	18.06 min	1055	1432	1556	1421	1366
1-chloro-2-hexanone	23.03 min	22453	28849	33181	26636	27779
1-chloro-2-hexanol	26.21 min	10212	13450	17083	13770	13629



Figure 2. Chromatograms showing the positional isomers of alkenones, the products of secondary reactions of alkenyl radicals, formed by H abstraction. (a-d) Heptenones with keto group at 4, 3, 5 and 6 positions, respectively; (e-i) octenones with ketogroups at 5, 4, 6, 3, and 7 positions, respectively; (j-o) nonenones with ketogroups at 5, 6, 4, 3, 7 and 8 positions, respectively.

Table	2. Con	nparison	of Yields	of the	Products	Based	on	the
Areas	under	the Chro	omatograi	ns				

parent molecule	ratio of areas 1-chloro ketone to 1- chloroalcohol	ratio of enones with keto group at different carbon atoms, C3/C4/C5/ C6/C7/C8
1-butene	3.5	only one isomer
1-hexene	2.0	1:0.5:1.6
1-heptene	2.1	1:0.3:1.9:1.8
1-octene	2.8	1:0.4:1.6:2: 1.7
1-nonene	2.5	1:0.7:3.2:2.7:2.9:2.0

The observed distribution of products may directly be attributed to the difference in the reactivity of different carbon atoms toward Cl atom. This possibility is discussed below on the basis of the rate coefficients of individual channels of addition and abstraction of H from different carbon atoms, computed theoretically.

3.2. Electronic Structures and Energetics: Reaction of 1-Heptene with Chlorine Atom. Detailed calculations were carried out with 1-heptene, where all the products have been well characterized experimentally. A very large number of rotational isomers is possible for 1-heptene, corresponding to a rotation of 60° or its multiples about one or more C–C bonds. Of these, only seven could be optimized and the lowest energy isomer was the one where the adjacent carbon atoms have staggered configurations due to steric repulsion (Figure 3). This is very similar to the structure, theoretically optimized as well as observed, in the case of 1-hexene.³⁴ The energy data indicates that more than one conformer will be present at room temperature. However, the attempts to optimize transition states from other conformers were not successful. Because the carbon atoms in all the conformers are in a very similar environment, the rate coefficients are not expected to be very different in all the conformers. Thus, the values obtained using the TSs optimized from the lowest energy conformer are only considered here. The optimized structures of the seven rotamers and their energies are given in Supporting Information (Figure S1).

The geometries of the reactants, prereactive complexes, transition states, and products of all the possible channels of reaction were optimized at MP2/6-311+G(d,p) level of theory and are shown in Figure 3. The numbering followed for the transition states (TSs) is shown below. The potential energy diagram showing the barrier heights and product energies computed at MP2/6-311+G (d,p) level of theory are shown in Figure 4. All the structural parameters, vibrational frequencies of reactants, prereactive complexes, transition states and products are given in the Supporting Information. (S.1.1–S.1.53 and S.2.1–S.2.8). The barrier heights and other thermodynamic parameters such as Gibbs free energy, entropies and heat of reactions are computed at MP2/6-311+G (d,p) level of theory and are given in S.3.



1-heptene

Two addition channels are possible, via transition states labeled as TS1a (addition at terminal carbon) and TS2a (addition at second carbon), both having energies lower than the reactants. These submerged transition states are formed via prereactive complexes, RC1a and RC2a, corresponding to the addition channel of chlorine atom at C1 and C2, respectively. These two prereactive complexes are found to be energetically identical, but differ structurally, as the addition happens at two different carbon atoms connected via the double bond. The potential energy level diagram for all these reactions with all the stationary points is shown in Figure 4. The two addition channels lead to the formation of products P1a and P2a, which



Figure 3. continued



Figure 3. Optimized geometries of the reactant, transition states of different addition and abstraction channels, prereactive complexes, product complexes, and products. The obtained bond lengths (Å) are given on structures computed at MP2/6-311+g(d,p) level of theory. Reddish brown represents carbon atoms, green represents hydrogen atoms, and blue represents chlorine atoms.

are much lower in energy as compared to the products of abstraction reaction.

Abstraction of H atom is possible from all the seven carbon atoms and the most important parameters that have to be considered during the formation of the corresponding transition states are the C–H bond length of the leaving hydrogen and newly formed bond between leaving hydrogen and Cl atom. Thus, the breaking C–H bond length is varied between 19 and 39% when compared with normal C–H bond length in 1-heptene. The 14 hydrogen abstraction channels in 1-heptene lead to the formation of products P1-P14 via transition states TS1-TS14 respectively, as shown in Figure 4. Although products of each individual H atom are shown in Figure 3, the energy of the most stable conformer is represented in Figure 4. It can be seen from Figure 4 that the abstraction of H atoms from C4 to C6 also passes through submerged transition states. The rate coefficients for all the abstraction channels, calculated using CTST, are given in Table



Figure 4. Potential energy level diagram for the reaction of 1-heptene with chlorine atom at MP2/6-311+g(d,p) level of theory.

Table 3. Rate Coefficients Calculated Using TST (in cm ³ molecule ⁻¹ s ⁻¹) for Individual Reaction Channels of 1-Heptene + Cl-
Products in the Temperature Range of 200-400 K at MP2/6-311+g(d,p) Level of Theory

T(K)	TS1	TS	2 7	ГS3	TS4	TS5	TS6	TS7
200	1.14×10^{-28}	3.06 ×	10 ⁻²⁹ 1.51	$\times 10^{-22}$	1.02×10^{-15}	2.61×10^{-14}	4.74×10^{-12}	1.42×10^{-12}
225	7.34×10^{-27}	$2.27 \times$	10 ⁻²⁷ 2.02	$\times 10^{-21}$	2.39×10^{-15}	4.24×10^{-14}	4.33×10^{-12}	1.49×10^{-12}
250	2.09×10^{-25}	7.28 ×	10 ⁻²⁶ 1.65	$\times 10^{-20}$	4.80×10^{-15}	6.40×10^{-14}	4.11×10^{-12}	1.57×10^{-12}
275	3.30×10^{-24}	1.26 ×	10 ⁻²⁴ 9.32	$\times 10^{-20}$	8.66×10^{-15}	9.11×10^{-14}	4.01×10^{-12}	1.67×10^{-12}
300	3.33×10^{-23}	1.38 × 1	10 ⁻²³ 4.01 2	× 10 ⁻¹⁹ 1	1.44×10^{-14}	1.24×10^{-13}	3.99×10^{-12}	1.79×10^{-12}
325	2.39×10^{-22}	1.06 ×	10 ⁻²² 1.40	$\times 10^{-18}$	2.24×10^{-14}	1.64×10^{-13}	4.03×10^{-12}	1.92×10^{-12}
350	1.31×10^{-21}	6.18 ×	10 ⁻²² 4.13	$\times 10^{-18}$	3.31×10^{-14}	2.10×10^{-13}	4.11×10^{-12}	2.07×10^{-12}
375	5.81×10^{-21}	2.88 ×	10 ⁻²¹ 1.07	$\times 10^{-17}$	4.69×10^{-14}	2.64×10^{-13}	4.23×10^{-12}	2.23×10^{-12}
400	2.15×10^{-20}	1.11 ×	10^{-20} 2.47	$\times 10^{-17}$	6.44×10^{-14}	3.25×10^{-13}	4.38×10^{-12}	2.40×10^{-12}
T(K)	TS8	TS9	TS10	TS11	TS12	TS13	TS14	total k by abstraction
200	2.21×10^{-10}	1.89×10^{-11}	9.02×10^{-10}	1.41×10^{-10}	1.46×10^{-15}	1.46×10^{-15}	2.26×10^{-14}	1.29×10^{-09}
225	1.32×10^{-10}	1.48×10^{-11}	4.60×10^{-10}	8.83×10^{-11}	3.27×10^{-15}	3.28×10^{-15}	3.74×10^{-14}	7.01×10^{-10}
250	8.89×10^{-11}	1.24×10^{-11}	2.74×10^{-10}	6.20×10^{-11}	6.37×10^{-15}	6.38×10^{-15}	5.71×10^{-14}	4.43×10^{-10}
275	6.56×10^{-11}	1.10×10^{-11}	1.82×10^{-10}	4.72×10^{-11}	1.12×10^{-14}	1.12×10^{-14}	8.22×10^{-14}	3.12×10^{-10}
300	5.17×10^{-11}	1.00×10^{-11}	1.32×10^{-10}	3.83×10^{-11}	1.82×10^{-14}	1.82×10^{-14}	1.13×10^{-13}	2.38×10^{-10}
325	4.28×10^{-11}	9.43×10^{-12}	1.02×10^{-10}	3.25×10^{-11}	2.78×10^{-14}	2.78×10^{-14}	1.50×10^{-13}	1.93×10^{-10}
350	3.69×10^{-11}	9.06×10^{-12}	8.25×10^{-11}	2.86×10^{-11}	4.05×10^{-14}	4.05×10^{-14}	1.94×10^{-13}	1.64×10^{-10}
375	11	0.04 × 10-12	6.05×10^{-11}	2.58×10^{-11}	5.67×10^{-14}	5.67×10^{-14}	2.45×10^{-13}	1.44×10^{-10}
	3.28×10^{-11}	8.84 X 10	0.95 X 10	2.30×10	5.07 × 10	5.07 × 10	2.43 × 10	1.44 × 10

3. Each H atom abstraction is considered separately with a degeneracy (l) value of 1. On the basis of these rate coefficients, the abstraction channels via TS1, TS2, and TS3 can be neglected. The calculated rate coefficients of addition at C1 and C2 along with total rate coefficients are shown in Table 4, which shows clearly that the addition reaction is more feasible than the abstraction channels. The percentage contribution computed for significant channels is shown in Table 5. The temperature dependence of the total rate coefficient is given by

the expression $k_{1\text{-heptene+Cl}}$ (200–400 K) = (2.24 ± 0.79) × $10^{-12} \exp[(1786.1 \pm 98.6)/T]$ cm³ molecule⁻¹ s⁻¹. The theoretically computed total rate coefficient at 300 K, 7.74 × 10^{-10} cm³ molecule⁻¹ s⁻¹, is close but higher than the experimentally determined value of 4.4×10^{-10} cm³ molecule⁻¹ s⁻¹ at 298 K. Because VTST method is known to be more appropriate in the case of reaction with very low lying transition states, this was also carried out. But the computed rate coefficients were found to be high of the order of 10^{-9} to 10^{-8}

Table 4. Rate Coefficients (in cm^3 molecule⁻¹ s⁻¹) of the Reaction Due to the Addition of Cl at C1, C2 Sites and the Total Abstraction of H Atoms from All the Possible Sites

T(K)	rate coefficient for addition at C1 (Ts1a)	rate coefficient for addition at C1 (Ts2a)	total rate coefficient by addition	total rate coefficient by abstraction	total rate coefficient
200	1.52×10^{-08}	3.39×10^{-09}	1.86×10^{-08}	1.29×10^{-09}	1.99×10^{-08}
225	4.52×10^{-09}	1.10×10^{-09}	5.62×10^{-09}	7.01×10^{-10}	6.29×10^{-09}
250	1.74×10^{-09}	4.52×10^{-10}	2.19×10^{-09}	4.43×10^{-10}	2.61×10^{-09}
275	7.86×10^{-10}	2.21×10^{-10}	1.01×10^{-09}	$3.12 \times 10 - 10$	1.32×10^{-09}
300	4.14×10^{-10}	1.22×10^{-10}	5.36×10^{-10}	2.38×10^{-10}	7.74×10^{-10}
325	2.42×10^{-10}	7.50×10^{-11}	3.17×10^{-10}	1.93×10^{-10}	5.10×10^{-10}
350	1.54×10^{-10}	4.96×10^{-11}	2.03×10^{-10}	1.64×10^{-10}	3.67×10^{-10}
375	1.04×10^{-10}	3.48×10^{-11}	1.39×10^{-10}	1.29×10^{-09}	2.83×10^{-10}
400	7.44×10^{-11}	2.57×10^{-11}	1.00×10^{-10}	7.01×10^{-10}	2.31×10^{-10}

Table 5. Computed Percentage Contribution of Addition at Terminal Carbon (TS1a), at Second Carbon (TS2a), and Abstraction Channels from C5 Onwards (TS8–TS14) to the Total Rate Coefficient for the Reaction of Cl Atom with 1-Heptene over the Temperature Range of 200–400 K

temp. (K)	TS1a	TS2a	TS8	TS9	TS10	TS11	TS12	TS13	TS14
200	76.44	17.07	1.11	0.10	4.54	0.71	7.3×10^{-6}	7.4×10^{-6}	1.1×10^{-4}
225	71.38	17.48	2.10	0.24	7.32	1.40	5.2×10^{-5}	5.2×10^{-5}	5.9×10^{-4}
250	65.68	17.33	3.41	0.48	10.51	2.38	2.4×10^{-4}	2.4×10^{-4}	2.2×10^{-3}
275	59.60	16.73	4.97	0.83	13.84	3.58	8.5×10^{-4}	8.5×10^{-4}	6.2×10^{-3}
300	53.43	15.82	6.68	1.30	17.05	4.94	2.3×10^{-3}	2.4×10^{-3}	1.5×10^{-2}
325	47.45	14.71	8.40	1.85	19.98	6.37	5.5×10^{-3}	5.5×10^{-3}	2.9×10^{-2}
350	41.86	13.51	10.07	2.47	22.49	7.78	1.1×10^{-2}	1.1×10^{-2}	5.3×10^{-2}
375	36.77	12.30	11.60	3.12	24.56	9.12	2.0×10^{-2}	2.0×10^{-2}	8.6×10^{-2}
400	32.24	11.14	12.97	3.79	26.21	10.35	3.3×10^{-2}	3.3×10^{-2}	1.3×10^{-1}

Scheme 1. Addition of Cl Atom to 1-Alkenes



 cm^3 molecule⁻¹ s⁻¹, as shown in the Supporting Information, S.4.

4. DISCUSSION

In the experimental conditions employed for studying Cl atominitiated reactions of VOCs in air, there is a possibility of generation of OH through the reactions of peroxy radicals³⁵ and this may also influence the observed products. However, our earlier studies on determination of the rate coefficients of reactions of Cl with 1-alkenes in the presence of air indicated the absence of any significant OH generation under the present experimental conditions.¹⁷ Typical products of addition of OH to 1-alkenes were also not observed here. Hence it appears that the observed products are entirely due to the secondary reactions of the radicals generated by the reactions of Cl with 1alkenes. The reactions following the addition and abstraction channels, leading to the major observed products b with ketoand alcohol groups at different carbon atoms, can be represented by the reactions given in Schemes 1 and 2, respectively. Ketones may be generated by disproportionation reaction of the peroxy radicals as well as via alkoxy radicals, which may be responsible for their higher yield as compared to the corresponding alcohols. Similar formation of ketones and alcohols is known to be the major reaction of the corresponding peroxy radicals in the case of alkanes³⁶ in the absence of NOx along with hydroperoxides. Formation of hydroperoxide is a possible channel in the present conditions also. They are thermolabile and will not be detected by GC/ MS. At the injection temperature of 200 °C, large hydroperoxides are reported to undergo dissociation reaction to form alcohols and ketones.³⁷ However, this involves carbon-carbon scission on either side of the alkoxy radical intermediate produced from hydroperoxides. Hence the hydroperoxides may influence the yield of smaller aldehydes and ketones, but chloroketones/alcohols and alkenyl ketones/alcohols where the carbon chain of the parent molecule is intact is not expected to be formed from hydroperoxide during sampling or analysis. Thus, the observed distribution pattern of long chain alcohols

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Scheme 2. Abstraction of H Atom by Cl Atom from 1-Alkenes



and ketones in which the carbon chain of the parent molecule is intact is expected to be comparable to the pattern based on the theoretically obtained rate coefficients of the individual channels, highlighting the important channels of reactions. The major deviations may indicate the most probable secondary reactions of the radicals. A detailed analysis of the observed products and comparison with the existing literature data is given below.

There has been one report on the products of Cl atom reaction with 1-butene.³⁸ Chloroacetaldehyde ($20 \pm 3\%$), CH_2O (7 ± 1%), and CO_2 (4 ± 1%) have been identified and the yield of 1-chloro-2-butanone, the major product of Cl addition, is assessed to be around 30% in the presence of NOx.³⁸ Chloroacetaldehyde, suggested to be formed by the dissociation of 1-chlorobutoxy radical, is observed in the present study also as one of the major products in the Cl initiated oxidation of 1-butene but it is absent in the case of higher alkenes.¹⁷ The present experimental observation of chloroketones and chloroalcohols as the major products confirms the addition of Cl at the terminal carbon to be the major channel of reaction in 1-butene as well as in all the higher alkenes, which matches with the computational results (Table 3). There is no direct experimental evidence of products of addition at C2 position, whereas computational results in the case of 1-heptene indicate almost 15% of the reaction to proceed via addition at C2 at room temperature (Table 5). Thus, 2-chloro-1-alkyl radical, if formed, appears to be dissociating to smaller fragments, unlike 1-chloro-2-alkyl radical, or their formation is much smaller than whatever is predicted.

Positional isomers of alkenones and alkenols are observed in all the 1-alkenes from 1-butene to 1-nonene, which have to be formed directly or indirectly from the corresponding alkenyl radicals generated by H abstraction reaction¹⁷ (Scheme 2). The earlier experimental study on 1-butene³⁸ does not report any abstraction products. However, abstraction of H atom from allyl carbon is identified as a significant channel in the reaction

of isoprene with Cl atom based on the kinetics as well as HCl yield²⁰ accounting for ~15% of the reaction. This study²⁰ suggests the abstraction reaction to be a complex process, involving initial adduct formation followed by HCl elimination. Experimental dynamics studies at low pressures as well as theoretical calculations on addition-elimination reaction of Cl atom with alkenes have been reported recently^{25,39} that suggest the occurrence of roaming mechanism. However, under the present experimental conditions at atmospheric pressure the major pathway in small alkenes such as propene is expected to be addition, and whatever small percentage of abstraction products are formed are by direct H atom abstraction.⁴⁰ Additionally the absence of any shift in the position of the double bond in the observed products of 1-alkenes also does not support the possibility of addition followed by elimination reaction.

The results of the present theoretical calculations show that oxidation at allyl position is the most favored channel thermodynamically. But the computed rate coefficients of abstraction reactions are found to follow the order of the transition state barriers (Figure 3), being negligible at allyl position and increasing as the position is away from the double bond. The rate coefficient of abstraction computed at C5 and C6 are of similar order as the experimental rate coefficient of H atom abstraction by Cl atom in alkanes. The product distribution, consistently observed in all the higher alkenes, also shows abstraction of H atom to be more dominant at carbon atoms away from the double bond, being partially in agreement with the computational results. However, there is a difference in the abstraction at allyl position with the observed probability being much higher than that predicted computationally. Also, the computational results predict the abstraction probability from C5 to the carbon next to the terminal carbon to increase consistently, whereas the product study shows the yields of the products of abstraction of the respective abstraction products to be very similar and almost twice that of the radical at allyl position. For example, the ratio of enones,

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1-hepten-3-one (at C3), 1-hepten-4-one (at C4), 6-hepten-3one (at C5), and 6-hepten-2-one (at C6) is found to be 1:0.33:1.9:1.8. (This relative ratio of the yields in Table 2 is only for alkeneones, and expected alkenal from terminal carbon atom, as shown in Scheme 2, is not included as the yield was low and quantitative comparison was not possible, being a different functional group.) But the calculated percentage contributions are 8% at C5 (TS8 and TS9), 22% at C6 (TS10 and TS11), and negligible at other carbon atoms (Table 5). The deviation is even more in the ratios based on VTST calculations (see Supporting Information, S4), 1.2% and 3.9%, respectively, at C5 and C6 with the contribution at C6 being almost 3 times that at C5 and negligible at other carbon atoms.

The contradiction of the present computationally obtained relative ratios with the experimentally observed product distribution may arise due to different reasons. It is possible that the primary radical, formed at the particular carbon atoms that are kinetically dictated, undergoes H atom exchange with other molecules of alkenes, resulting in the formation of radicals at all the carbon atoms. In that case, the consistent pattern of the position of oxidation, observed in all the alkenes, must reflect the thermodynamic stability of the radicals. But hepten-3-one is not the most abundant product, though allyl radical is the most stable radical (Figure 4). Efficient isomerization of the initially formed alkenyl radical or the corresponding peroxy/alkoxy radicals may also be a possibility, leading to all the positional isomers. However, the present limitation of considering only one rotamer for the computational studies may limit the validity of the rate coefficients and the computed product distribution. In any case, the contradictions observed between the experimental product distribution and that expected based on the calculations undoubtedly point out to either some interesting aspects of secondary chemistry of the radicals or the shortcomings in the present theoretical calculations of the fast reactions of Cl atoms with these alkenes.

Interestingly, the H atom abstraction product ratio is closer to the rate coefficient ratio predicted by the SAR developed by Ezell et al., except for the abstraction from C4. Abstraction from all the carbon atoms was considered to be feasible with the reactivity of allyl H atom being lower at almost half of that of the secondary alkyl groups. The yield of products with ketogroup on C5-C8 was found to be 1.6-2 times that of ketones at C3 position except in 1-nonene, where the ratio is higher (Table 2). Abstraction rate coefficients of all the other secondary alkyl groups are predicted to be similar, which matches with the almost identical yield, experimentally observed for 6-hepten-3-one (at C5) and 6-hepten-2-one (C6) (Table 1). This similarity of product distribution with the SAR, developed based on the observed rate coefficients, implies it to be kinetically dictated. The deviation at C4, which is highest in energy (Figure 3), may indicate either dissociation of the C4 radical or its peroxy/alkoxy radical to form allyl fragment. This is supported by the presence of propenal and the relatively high abundance of aldehyde with the number of carbon atoms lower by three in all the alkenes, for example, butanal in 1-heptene.¹⁷ The areas of smaller aldehydes do not increase for higher alkenes in spite of the increase in ECN, indicating that their yields are decreasing as the number of carbon atoms increase. This supports the earlier observation in the case of OH reaction⁴¹ that the probability of dissociation of the alkyl/alkoxy radicals decreases with the increasing chain length of the parent 1-alkene. Also, as the number of carbon

atoms increase, the fractional yield of the dissociating C4 radical is expected to decrease, which may also be responsible for decreasing yield of lower aldehydes with increasing carbon number. The dissociation appears to be mainly from the alkenyl radical, not from the chloroalkyl radicals, because smaller chloroaldehydes were absent among the products of higher 1-alkenes.

5. CONCLUSION

A systematic study on the products of reactions of Cl atom with 1-alkenes, both addition and H atom abstraction, has been carried out in the presence of air. The product distribution observed here reflects the situation in the atmosphere only partly, being relevant only in NOx free condition. However, the observations are important in understanding the Cl atom reactivity. A computational study on the kinetics of the reactions of each individual channel has also been carried out, with 1-heptene as a typical case to understand the experimentally observed product pattern. Both the theory and experiments conclude the dominant reaction channel to be the addition of Cl to the terminal carbon atom. However, the computational results overestimate the rate coefficients of addition as well as that of abstraction from C6 and underestimate the rate coefficient of abstraction at C5. The experimental results support the earlier observation by Ezell et al. that the rate coefficient of allylic H atom abstraction is small as compared to the rate coefficient of alkyl secondary H atom abstraction. On the other hand, the theoretical results totally rule out abstraction from allyl carbon, which contradicts with the experimental observations as well as SAR prediction by Ezell et al. This is probably due to the inadequacies of the present computational method in understanding these reactions of Cl, which are very fast. The only mismatch of the experimental results with the SAR prediction is in the case C4, which is attributed to the dissociation of the C4 alkyl/ alkoxy radical leading to allyl radical, finally resulting in propenal and an aldehyde with three carbon atoms less than the parent alkene. The fact that the product distribution can be explained by the SAR, developed from experimental rate coefficient data, implies it to be kinetically dictated. The deviation in the case of C4 emphasizes the importance of secondary reactions.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.6b04667.

Structural parameters in the form of Cartesian coordinates and vibrational frequencies of all the optimized geometries are given.(PDF)

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