

Kinetics and Degradation Mechanism of Atmospheric Isoprene (2-methyl-1, 3-butadiene (C₅H₈)) with Chlorine Radical and Its Derivatives – A DFT Study

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Abstract

Isoprene (2-methyl-1, 3-butadiene (C₅H₈)) is one of the most prominent and abundant non-methane hydrocarbon existing in the lower level of the troposphere. In this work, possible reaction mechanism of chlorine (Cl) radical initiated isoprene and its subsequent reactions are investigated using quantum chemical methods. The calculated thermodynamic result shows that the reaction of isoprene with the Cl radical at the terminal C=C bond position plays an important role to predict the end products. The calculated rate coefficient for the reaction between isoprene and Cl radicals (Cl addition at C1, C3, C4 and C5 positions) is found to be 4.89×10^{-11} , 6.91×10^{-10} , 1.63×10^{-10} and 8.12×10^{-10} cm³/molecule/sec at 298K. The branching ratio and atmospheric lifetime have been calculated from the reaction rate coefficient values of isoprene+Cl. The reaction force analysis predicts Cl radical addition at the terminal C=C bond position plays a dominant role by structural rearrangement. The kinetic and thermodynamic results reveal that the electrophilic addition of Cl radical to the terminal carbon atom plays the dominant role in the marine boundary. Further, the subsequent reaction of Cl-isoprene adduct radical helps for the development of ozone layer during daytime.

Introduction

The reactions of non-methane hydrocarbons (NMHCs) with atmospheric oxidizing species (such as hydroxyl (OH) radical, nitrate (NO₃) radical, ozone (O₃) molecule and chlorine radical (Cl)) are most important in the earth's troposphere and these contribute to the formation of secondary organic aerosols (SOAs)^[1-4]. Among such non-methane hydrocarbons, isoprene (2-methyl-1, 3-butadiene (C₅H₈)) is one of the most prominent and abundant non-methane hydrocarbon existing in the lower level of the troposphere which is released into the atmosphere through various biogenic and anthropogenic processes^[5,6]. Like methane, the excretion of isoprene in the world is around 500-600 Tgc year⁻¹ due to the unfinished combustion of diesel fuels, gasoline, automobile exhausts, petroleum refining, plastic, or rubber industries and other biogenic volatile organic compounds (BVOCs)^[7-9]. Due to this excessive emission, isoprene plays a central role in the tropospheric chemistry related to air quality and climate change. The abundant isoprene in the atmosphere undergoes several chemical processes, which is leading to their potential removal from the atmosphere and transformation processes in the atmosphere. Especially, oxidation processes can reduce the atmospheric lifetime of biogenic isoprene in the daytime and it contributes to the formation of secondary organic aerosols (SOAs)^[10].

For the last few decades, there are several experimental and theoretical studies have been reported on the kinetics of reactions of isoprene with atmospheric oxidants. M.L. Ragains and B.J. Finloyson Pitts have experimentally studied the kinetics and mechanism of the reaction of Cl atom with isoprene at 760 Torr and 298K using relative rate techniques^[11]. Another important experimental study on isoprene was done by Yuri Bedjanian et al., where they studied the kinetics of the reaction of isoprene+Cl and obtained the overall

rate coefficient over the temperature range of 233-320 K at 1 Torr^[12]. Inseon Suh and Renyi Zhang have investigated the degradation mechanism of Cl initiated isoprene and measured the rate constant between Cl atom and isoprene is $(4.0 \pm 0.3) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 5 to 10 Torr and 298K^[13]. Subsequently, Inseon Suh et al. both experimental and theoretically study the reaction of isoprene+NO₃ and they measured the rate coefficient in the pressure range of 5-7 Torr at 298+2K using chemical ionization mass spectrometry (CIMS) detection^[14]. Recently, Victoria P. Barber et al reported the formation of four carbon criegee intermediate from ozonolysis of isoprene^[15]. Earlier this year, a theoretical investigation on isoprene was done by Xirui Guo et al., where they studied the reaction of isoprene with Cl radical and the reaction rate constants for tight and loose transition states were calculated by RRKM theory and canonical variational transition state theory (CVT) respectively^[16]. From the earlier literature, the OH radicals and O atoms are well known most important oxidants in the troposphere, which are responsible for the removal of VOCs in the atmosphere. Meanwhile, Cl radicals are also highly reactive in the coastal and marine boundaries. This highly reactive Cl radical is produced in the marine boundary as a consequence of both direct emission and chemical processes. Generally, particle bound chlorine released into the gas phase through heterogeneous processes on particulate surfaces or sea salt aerosols. Recently, Luo et al reported that the emission of Cl radicals from seawater is estimated to be 1792.6 Tg Cl yr⁻¹^[17] and it is comparably higher than that of other sources (such as dust 15 Tg Cl yr⁻¹ and volcanic eruptions 2 Tg Cl yr⁻¹). Therefore, in the present study aimed to investigate the degradation of isoprene with Cl radical along with their intermediates, transition states and product radicals in the presence of O₂, NO and H₂O molecules. The earlier investigation mainly focused on primary reaction of isoprene with Cl radical which hinders the understanding of secondary reactions from Cl radical initiated isoprene and formation of SOAs from Cl radical initiated isoprene. A detailed theoretical study on the kinetics of Cl initiated isoprene and the secondary reaction is yet to be known. Therefore, in this work, a quantum chemical study is used to understand the initial and subsequent reaction of isoprene+Cl. The canonical variational transition (CVT) state theory^[18] including small curvature tunneling (SCT)^[19] is used to calculate the relative rate coefficient for the reaction of isoprene+Cl. The obtained rate coefficients are used to determine the lifetime of isoprene for the removal of Cl radicals. In addition to that, the reaction force analysis is also calculated to find out the structural fate of the reaction and their results are correlated with the relative energy profile in the present work.

Computational details

The geometric parameters of all the reactants, transition states, intermediates, and products involved in the proposed reaction mechanism are optimized using M06-2X functional and 6-311+G* basis set. The above-mentioned hybrid meta-generalized gradient-approximations (hybrid meta-GGAs) M06-2X is recommended for studying thermochemistry, kinetics, noncovalent interactions^[20-23]. The corresponding harmonic vibrational frequency calculations are performed to identify the nature of stationary points on the potential energy surface using the same level of theory^[24]. The local minima are confirmed with the real frequency in all reactants, intermediates and product structures, whereas the corresponding transition structure has only one imaginary frequency. Further, the reaction path is calculated through intrinsic reaction coordinates (IRCs)^[25] to find the right transition states which connect the two equilibrium structures^[26]. To obtain more accurate relative energies, the single point energy is carried out using CCSD (T)^[27] functional and 6-311+G* level of theory. Thermodynamic properties enthalpy (ΔH), entropy (ΔS) and Gibbs free energy (ΔG) are calculated by including a thermodynamic correction to the potential energy surface at 298.15 K and 1 atmospheric pressure. All the electronic structure calculations are performed using Gaussian 09 program package^[28]. In this study, the kinetic rate constants are calculated by the canonical variational transition (CVT) state theory^[18] including small curvature tunneling (SCT)^[19] over the temperature range of 278-350 K which are performed at M06-2X/6-311+G* level of theory.

Fukui functional analysis

The Fukui function is one of the most important concepts in Density Functional Theory (DFT). It is widely used to predict active sites and provides information about local site reactivity within the molecule. The Fukui function can be defined as,

$$f = \left(\frac{\partial \rho(r)}{\partial N} \right)_v \quad (1)$$

Where N is the number of atoms within the molecule, $\rho(r)$ is electron density in the partial derivatives, v represents the external potential. Due to discontinuity, this equation cannot be evaluated directly^[29,30]. Hence, the following modified equation is used for calculating Fukui function^[31]

$$f_k^+ = [q(n+1) - q(N)] \text{ For nucleophilic attack } (2)$$

$$f_k^- = [q(N) - q(n-1)] \text{ For electrophilic attack } (3)$$

$$f_k^0 = \frac{1}{2} [q(n+1) - q(n-1)] \text{ For radical attack } (4)$$

Where +, -, and 0 signs denote the nucleophilic, electrophilic and radical attack.

Reaction force analysis

A chemical reaction is mainly expressed in terms of geometrical changes of structural parameters and rearranging of the electron densities involved in the chemical process. But, the relative energy profile does not give us complete information about the chemical reaction. Hence, the reaction force concept is applied for finding structural and electronic changes existing along the complete chemical reaction process^[32-35]. The reaction force $F(\xi)$ ^[36] is defined as

$$F(\xi) = -\frac{\delta E}{\delta \xi} \quad (5)$$

On the other hand, the reaction force profile provides an energy partition of the activation and reaction energies $\Delta E^\ddagger$ and ΔE respectively. Therefore $(\Delta E^\ddagger)$ and (ΔE) takes the following form^[37-39]

$$(\Delta E) = W_1 + W_2 + W_3 + W_4 \quad (6)$$

$$(\Delta E^\ddagger) = W_1 + W_2 \quad (7)$$

From equation (6) and (7), W_1 , W_2 , W_3 , and W_4 are the reaction works involved in the mechanism.

$$W_1 = - \int_{\xi_R}^{\xi_1} F(\xi) d\xi > 0$$

$$W_2 = - \int_{\xi_1}^{\xi_{TS}} F(\xi) d\xi > 0$$

$$W_3 = - \int_{\xi_{TS}}^{\xi_2} F(\xi) d\xi < 0$$

$$W_4 = - \int_{\xi_2}^{\xi_p} F(\xi) d\xi < 0$$

Results and discussion

The reaction mechanism of chlorine radical initiated isoprene is analyzed through four different pathways and its subsequent reactions shown in **Scheme 1**. The geometry of the reactant, transition states, intermediates and products for the above mentioned reaction mechanism are calculated at M06-2X/6-311+G* level of theory. The corresponding harmonic vibrational frequency calculations are achieved by the same level of theory and all transition states are confirmed by using IRC calculation. In addition to that, a single point energy calculation for the involved reaction mechanism is carried out by CCSD (T)/6-311+G* level of theory. The calculated condensed Fukui function values are used to find the most favorable active site in the reactant by the nucleophilic(f_k^+), electrophilic(f_k^-) and radical(f_k^0) attack and their corresponding values are listed in supplementary (**Table S1-S4**).

Formation of Cl-isoprene adduct radicals

Isoprene can react with Cl radical at the C=C double bond positions such as C1, C3, C4, and C5 which lead to the formation of Cl isoprene adduct radical (C_5H_8Cl) intermediates (I1a, I1b, I1c, and I1d) and their optimized structures are shown in **Figure 1**. The intermediates I1a, I1b, I1c, and I1d are formed along with the activation energy values of 7.63, 13.57, 12.14 and 13.14 kcal/mol respectively and their corresponding relative energy profile is shown in **Figure 2**. In isoprene, the condensed Fukui function value of C3, C1, C4,

and C5 atoms are found to be 0.051, 0.038, -0.016, and -0.025 respectively. In the Cl radical, the condensed Fukui function value is found to be 0.043. During the formation of Cl isoprene adduct radical intermediates (I1a, I1b, I1c and I1d), the obtained condensed Fukui function value shows that the nucleophilic carbon C3, C1, C4 and C5 atoms tend to interact with the electron deficient electrophilic Cl radical. During this Cl radical addition, the π bond is cleaved homolytically in between the (C=C) atoms and it leads to form the covalent bond between (C—Cl) atoms. In the case of bond formation, the Cl radical able to accommodate the electron as a lone pair which can stabilize the structures by resonance delocalization. As shown in **Figure 1**, the intermediates I1a, I1b, I1c, and I1d are formed through the transition states TS1a, TS1b, TS1c, and TS1d, where the obtained single imaginary frequency values are -318.896 cm^{-1} , -241.151 cm^{-1} , -829.152 cm^{-1} , and -241.115 cm^{-1} respectively, confirms the transition state on PES by IRC calculations. During the addition of Cl radical at C1 position, the bond length of (C1—C2), (C1—C3) and (C1=C4) atoms are found to be 1.502 Å, 1.461 Å and 1.343 Å respectively. Whereas in the formation of intermediate I1a, the bond length of (C1—C2), (C1—C3) and (C1=C4) atoms elongated around 0.01 Å, 0.04 Å and 0.1 Å respectively. After that addition of Cl radical at C3 position, the bond length of (C3=C5), and (C3—C1) atoms are found to be 1.338 Å and 1.461 Å respectively. The previously reported bond length of C=C and C—C atoms are 1.33Å and 1.54Å respectively and these results are in good agreement with the obtained results [40]. During the formation of intermediate I1b, the bond length gets elongated around 0.128 Å and 0.042 Å. During Cl radical addition at C4 position, the bond length between C4 and C1 atoms are found to be 1.339 Å, while in the formation of intermediate I1c, the bond length is extended around 0.14 Å. In the formation of intermediate I1d, the bond length between C5 and C3 atom elongated around 0.15Å, The Cl—C bond distances in intermediates I1c and I1d are 1.83Å and 1.83Å respectively where the bond length of Cl—C atoms is very similar in both intermediates. Another two adduct radical intermediates I1a and I1b with Cl radical addition to the internal positions C1 and C3 atoms contain well localized double bonds and the Cl—C bond distances in intermediates I1a and I1b are 1.90Å and 1.88Å respectively, which is a little higher than those of the intermediates I1c and I1d with the terminal Cl radical addition. In the present work, the obtained bond length of C—Cl atoms is well correlated with the previously available experimental investigation [41]. As given in (**Table 1**), the formation of Cl isoprene adduct radical intermediates I1a, I1b, I1c, and I1d are found to be exothermic with the enthalpy (ΔH) values of -13.230, -13.852, -26.326, and -26.111 kcal/mol and these intermediates are also found to be exoergic with the Gibbs free energy (ΔG) values of -11.647, -13.100, -26.421, -25.231 kcal/mol respectively. The calculated thermodynamical values are well correlated with previous results [42] and the results are compared in (**Table 1**). The $\Delta H < 0$ and $\Delta G < 0$ reveals that the reactions are spontaneous and more feasible. The thermodynamic results reveal that the terminal addition of Cl radical with the isoprene is thermodynamically more favorable than the Cl addition of the internal positions (C1 and C3). Wenfang Lei and Renyi Zhang also reported that the Cl radical addition at terminal positions (C4 and C5) has lower enthalpy (ΔH) values than the Cl radical addition at the internal positions (C1 and C3) [43]. Hence, the Cl radical addition reaction reveals that the addition of Cl radical at the terminal position is thermodynamically more favourable in the marine boundary.

Formation of chloroalkenyl peroxy radical criegee intermediates

The Cl isoprene adduct radical intermediates I1a, I1b, I1c, and I1d lead to form a chloroalkenyl peroxy radical criegee intermediates I2a, I2b, I2c, and I2d by the addition of O_2 molecule and their optimized structures are shown in (**Figure 3**). The criegee intermediates I2a and I2d are formed with the activation energy values of 2.245, 2.594 kcal/mol respectively, I2b and I2c formed in a barrierless reaction and their relative energy profile are shown in **Figure 4**. These criegee intermediates are formed through the transition states TS2a, TS2b, TS2c, and TS2d with the single imaginary frequency values of -278.725 , -108.025 , -178.434 , and -341.418 cm^{-1} respectively. In Cl isoprene adduct radical intermediates (I1a, I1b, I1c, & I1d), the active sites are found to be at carbon (C4, C5, C1, and C3) positions and their obtained corresponding condensed Fukui function values are -0.439, -0.45, -0.267, and -0.265. These active sites tend to interact with the electron-rich nucleophilic oxygen O15 atom with the condensed Fukui function value of -0.046. During the O_2 addition at the C4 position, the bond length of (C4—O15), (C4—Cl) and (O15—O16) atoms are found to be 2.897 Å, 1.472 Å, and 1.189 Å respectively, While in the formation of intermediate I2a, the

bond length is elongated around 0.11Å, 1.46Å, and 0.06Å respectively. In O₂ addition at the C5 position, the bond length between C5—C3 atom is found to be 1.467 Å, while in the formation of intermediate I2b the bond length elongated around 0.05Å. During the addition of O₂ molecule at chiral carbon atom C1, the bond length of (C1—C3), (C1—C4), and (C1—C2) atoms are found to be 1.402Å, 1.479Å, and 1.496Å whereas in the formation of intermediate I2c the bond length lengthened around 0.1Å, 0.06Å, and 0.01Å respectively due to an increased σ nature of (C—C) bond. Simultaneously, the π bond is being transferred to the newly formed C—O₂ bond. At the time of O₂ addition at the C3 position, the bond length of (C3—C1), (C3—C5), and (C3—H9) atoms are found to be 1.399Å, 1.476Å, and 1.085Å respectively and in the formation of criegee intermediate I2d, the bond length become elongated around 0.1Å, 0.04Å, and 0.01Å respectively. During the formation of criegee intermediates, the bond angle decreases with increasing bond length due to the high electronegativity of Cl isoprene adduct radical intermediates I1a, I1b, I1c, and I1d. Thus, the formation of chloroalkenyl peroxy radical criegee intermediate I2a, I2b, I2c, and I2d are found to be exothermic with the enthalpy values of -30.523, -30.067, -17.498 and -17.430 kcal/mol and also found to be exoergic with the Gibbs free energy values of -26.308, -24.315, -12.544, and -13.9 kcal/mol respectively. The thermodynamically calculated enthalpy (ΔH) and Gibbs free energy (ΔG) values are compared with the previously available literature^[44], listed in (**Table 2**) . The negative values of enthalpy reveal that the reactions are spontaneous and more feasible. The spontaneity of the criegee intermediates in the atmosphere further leads to a subsequent reaction with NO or OH radical.

After that, the intermediates I2a, I2b, I2c, and I2d, the reactions occur with two different steps. As shown in **Scheme. 1**, one step is the formation of intermediates I3a, I3b, I3c, and I3d by the addition of NO radical and another step is the formation of intermediates I6, I6c, and I6d by decomposition.

Formation of chloroalkenylalkoxy radical intermediates

Under the atmospheric condition, chloroalkenyl peroxy radical criegee intermediates I2a, I2b, I2c, and I2d react with the presence of nitrogen monoxide (NO) radical possesses chloroalkenylalkoxy radical intermediates I3a, I3b, I3c, and I3d respectively and their optimized structure are shown in **Figure. 5**. As shown in **Figure. 6**, the intermediates I3a, I3b, I3c, and I3d are formed with the activation energy values of 24.786, 29.171, 30.775, and 29.493 kcal/mol respectively. During this reaction, the condensed fukui function analysis is used to find the active site of the chloroalkenyl peroxy radical criegee intermediates I2a, I2b, I2c, and I2d, where the active sites are found to be at terminal oxygen atom for each criegee intermediates. The condensed fukui function values are found to be -0.297, -0.187, -0.194 and -0.199 at the O16 position of each intermediates I3a, I3b, I3c, and I3d respectively, which tends to attract the electron-deficient electrophilic atom N17 with the condensed Fukui function value of -0.162. The NO radical addition reaction is observed through the transition states TS3a, TS3b, TS3c, and TS3d with the single imaginary frequency value of -110.945, -182.017, 88.346, and 210.912 cm⁻¹ respectively. The TSs are confirmed by IRC calculation through PES. During the NO radical addition reaction with the criegee intermediate I2a, the bond length of (O18—N17) and (O16—O15) atoms are found to be 1.1 Å and 1.4Å, whereas in the formation of intermediate I3a bond length extended around 0.01Å and 0.05 Å respectively. During the addition of NO radical with the intermediate I2b, the bond length of O15—O16 and N17—O18 atoms are found to be 1.4Å and 1.1Å and in the formation of intermediate I3b, the bond length elongated around 0.02Å and 0.08Å respectively. Similarly, the formation of intermediate I3c, the bond length of (N17—O18) and (O16—O15) atoms lengthened around 0.2Å and 0.02Å respectively. As shown in (**Table 3**) the formation of intermediate I3a, I3b, I3c, and I3d is endothermic with the enthalpy (ΔH) values of 23.741, 28.643, 30.495, and 30.599 kcal/mol and that they are endoergic with the Gibbs free energy (ΔG) value of 26.908, 30.893, 32.901, and 33.117 kcal/mol respectively which reveals that the reactions are less feasible and non-spontaneous. Further, the covalent bond between O15 and O16 atoms in an intermediates I3a, I3b, I3c, and I3d gets completely cleaved to form an intermediate I4a, I4b, I4c, and I4d respectively. As shown in (**Table 4**), the intermediates I4a, I4b, I4c, and I4d are formed in a barrier less reaction. During the formation of intermediate I4a, I4b, I4c, and I4d, the nitrogen dioxide (NO₂) eliminated into the atmosphere due to cleavage of the covalent bond between O15 and O16. In these steps, NO₂ elimination from respective intermediates are observed through the transition states TS4a, TS4b, TS4c, and TS4d. The reaction enthalpy for the elimination of NO₂ from

an intermediates I3a, I3b, I3c, and I3d are found to be exothermic with their corresponding values are -43.304, -37.914, -34.574, and -36.904 kcal/mol, and also the Gibbs free energies are found to be exoergic with the values of -41.848, -37.133, -34.118, and -36.941 kcal/mol respectively. By the negative values of the thermodynamic parameters of NO₂ elimination, the reactions are more feasible and spontaneous. Thus, the eliminated NO₂ helps to increase the level of ozone under atmospheric photo-oxidation.

As shown in **Figure 7**, intermediates I4a, I4b, I4c, and I4d undergoes decomposition to form four different product P1, P2, P3, and P4 as a SOAs through transition states TS5a, TS5b, TS5c, and TS5d which is confirmed by the IRC calculation. The product P1, P2, P3, and P4 are formed with the activation energy values of 7.635, 13.572, 6.231, and 13.143 kcal/mol respectively and it is shown in relative energy profile **Figure 8**. Both P1 and P2 are the products obtained from the addition of chlorine atom to C1 and C3 position respectively and they are formed by the homolytic bond fission between respective C—C atoms. Other end products of the isoprene reactions are P3 (methyl vinyl ketone (MVK)) and P4 (methacrolein (MACR)) and they are the potential end products obtained from the addition of chlorine atom to the terminal carbon C4 and C5 atoms. The addition of Cl atom at terminal position C4 and C5 also generates the CH₂Cl and it subsequently reacts to produce formyl chloride. As given in (**Table 4**), the thermodynamic parameters for the formation of end products P1, P2, P3, and P4 are found to be exothermic with the enthalpy values of -6.334, -0.539, -0.129, and -1.157 kcal/mol respectively. Moreover, they are found to be exoergic with the Gibbs free energy values of -10.353, -3.778, -5.479, and -2.189 kcal/mol respectively. From the thermodynamic results, the negative values reveal that the formation of product P1, P2, P3, and P4 are more feasible and spontaneous. During the formation of products, obtained entropy values 13.483, 10.858, 17.942, and 8.871 mol⁻¹ K⁻¹ are also indicated that the reactions are spontaneous and irreversible. The potential end products P1, P2, P3, and P4 are reactive in its own right and can contribute to O₃ production as well as provide a source of free radicals through their photolysis.

Reaction of criegee intermediates with H₂O

By the decomposition, the criegee intermediates I2a, I2b, I2c, and I2d are leads to produce CH₂Cl, CH₂OO radical, and chlorine containing hydrocarbons. The stabilized criegee intermediates CH₂OO, and two I6 intermediates are formed such as I6c and I6d, derived from chloroalkenylperoxy radical intermediates I2c and I2d respectively. Under the humid condition, CH₂OO reacts with H₂O leads to the formation of hydroxymethyl hydroperoxide (HMHP) intermediate I7a along with the activation energy values of 7.612 kcal/mol and it is shown in the relative energy profile **Figure 10**. This reaction is energetically more favorable and it is compared with previously available literature reported with the activation energy value of 8.1 kcal/mol [45]. The reaction between CH₂OO and H₂O starts with the formation of hydrogen-bond (COO[?](H₂O)) and it is shown in **Figure 9**. The existence of hydrogen bond has been recently pointed out by Aplincourt et al and Ramon Crehuet et al [45,46]. During the addition of H₂O, the bond length of (O4—O5) and (C1—O4) atoms are found to be 1.3Å and 1.2Å respectively and these found bond lengths are agreed well with the previously reported value of 1.3 and 1.2Å with other methods [47]. While in the formation of hydroxymethyl hydroperoxide (HMHP) intermediates I7a, the bond lengths increased around 0.05Å and 0.17Å respectively. Before the formation of HMHP, the reaction of CH₂OO with H₂O goes on through the TS7 and it is confirmed by the IRC calculation. As shown in (**Table 5**) the thermodynamic calculation for the formation of intermediate HMHP is found to be exothermic and exoergic with the enthalpy (ΔH) value of -41.501 kcal/mol and Gibbs free energy value of -0.063 kcal/mol respectively. From the thermodynamic parameters, negative values indicate that the reaction is feasible and more spontaneous. Thermodynamically obtained enthalpy and Gibbs free energy values are compared with the previously reported values of -40.7 kcal/mol and -41.3 kcal/mol respectively [45]. Finally, HMHP undergoes unimolecular decomposition to produce H₂CO+H₂O₂ with the activation energy value of 55.17 kcal/mol and it is compared with the previously available literature 48.1 kcal/mol [45]. As shown in **Figure 9**, the bond length of (O5—O4) and (C1—O7) atoms are found to be 1.417Å and 1.396Å respectively in HMHP and the bond length between (O5—O4) atoms elongated around 0.006Å due to the addition of hydrogen atom. Thermodynamic parameters for the formation of H₂CO+H₂O₂ are found to be endoergic and endothermic with the enthalpy (ΔH) value of 13.63 kcal/mol and the Gibbs free energy value of 10.63 kcal/mol respectively. The positive values of the

formation of $\text{H}_2\text{CO}+\text{H}_2\text{O}_2$ reveal that the reaction is less feasible and nonspontaneous. These results agree with the experimental observation^[48] that indicates only the formation of formic acid in the decomposition of HMHP. The obtained final by product in the present work is in good agreement with the previous experimental work^[48].

On the other hand in the presence of H_2O the formed intermediates I6b and I6c from chloroalkenylperoxy radical intermediates (I2c&I2d) lead to the formation of hydroxy hydroperoxide intermediates I7b and I7c with the activation energy values of 9.840 and -26.469 kcal/mol respectively. The reaction between intermediates (I7b & I7c) and H_2O starts with the formation of a hydrogen bond ($\text{COO}[\cdot]\text{H}_2\text{O}$) and it is shown in **Figure. 9**. During the addition of H_2O with intermediate I6b, the bond length of (C2—C1), (C3—C1), (C1—O11), and (O11—O12) atoms are found to be 1.475Å, 1.457Å, 1.261Å, and 1.377Å respectively, whereas, in the formation of intermediate I7b, the bond length become elongated around 0.04Å, 0.05Å, 0.16Å, and 0.04Å respectively. In the formation of I7b, the bond angle decreased around 13.8°, 10.50°, 8.49°, and 8.64° respectively. Further, the intermediate I7b decomposed to yield the product P6 (MVK) as a SOAs and H_2O_2 as shown in **Figure 9**. As shown in **Figure 11**, the product P6 is formed with the activation energy value of 47.877 kcal/mol. The product P6 is obtained through the transition state TS8b with a single imaginary frequency value of -1799.744 cm^{-1} and it is confirmed by IRC calculation. J.Fan et al^[49] and D. Huang et al^[50] also indicated the yield of MVK experimentally through decomposition and this result is in good agreement with the present work. During the formation of product P6, the calculated enthalpy (ΔH) and Gibbs free (ΔG) energy values are 6.219 and 2.369 kcal/mol which shows that the reaction is endothermic and endoergic. Based on thermodynamic parameters, the formation of MVK through the addition of H_2O is found to be less feasible and non-spontaneous compare to the formation of MVK in product P3.

During the addition of H_2O with intermediate I6c, the bond length of (C4—C1), (C3—C1), (C2—C1), and (O11—O12) atoms are found to be 1.3Å, 1.4Å, 1.5Å, and 1.3Å respectively whereas, during the formation of I7c, the bond length become elongated around 0.1Å, 0.06Å, 0.004Å, and 0.03Å respectively. Beyond this, the formed intermediate I7c decomposed to produce product P7 (MACR) as a SOAs and H_2O_2 . As shown in **Figure 11**, the product P7 is formed with the activation energy value of 48.427 kcal/mol and it is formed through the transition state TS8c with the single imaginary frequency value of -1805.916 cm^{-1} which is verified by the IRC calculation. As given in (**Table 5**), the formation of MACR is found to be endothermic with the enthalpy (ΔH) value of 7.794 kcal/mol and endoergic with the Gibbs free energy (ΔG) value of 3.615 kcal/mol. The calculated thermodynamic values revealed that the formation of end product P7 via intermediate I7c is less feasible and non-spontaneous when compared with the formation of end product P4 through Cl addition in the present work. Hence, the non-spontaneity of this reaction reveals that the water molecule could affect the properties of potential end products P6 (MVK) and P7 (MACR).

Kinetic analysis

According to the above discussed PESs, the formation of isoprene adduct radical leads to the formation of SOAs through subsequent reactions. The rate constants for the reaction between isoprene and Cl radicals are carried out over the temperature range of 278K-348K with an interval of 10K at 1 atm pressure. The CVT/SCT is used to calculate the rate constant for the formation of Cl isoprene adduct radicals (K_{1a} , K_{1b} , K_{1c} , & K_{1d}) at M06-2X/6-311+G* level of theory. The rate constant for the reaction of isoprene with Cl radical to C1, C3, C4, and C5 positions is found to be $4.89\cdot 10^{-11}$, $6.91\cdot 10^{-10}$, $1.63\cdot 10^{-10}$ and $8.12\cdot 10^{-10}$ $\text{cm}^3/\text{molecule}/\text{sec}$ respectively at 278K. At high-temperature 350K, the rate constant for the reaction of isoprene with Cl radical to C1, C3, C4, and C5 positions is found to be $6.38\cdot 10^{-11}$, $8.12\cdot 10^{-10}$, $7.52\cdot 10^{-10}$ and $8.83\cdot 10^{-10}$ $\text{cm}^3/\text{molecule}/\text{sec}$. These obtained rate constants K_{1a} , K_{1b} , K_{1c} , and K_{1d} are listed in(**Table 6**) and the obtained reaction rate constants are increased with increasing temperature which is displayed in **Figure 12**. In this study, the calculated rate constants for the primary Cl-isoprene adduct radical is feasible with the experimentally reported values of $5.55\cdot 10^{-10}$, $4.48\cdot 10^{-10}$ $\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ ^[42,51]. This result reveals that the reaction between Cl radical and isoprene is kinetically and thermodynamically more favorable in the marine boundary.

The branching ratios are calculated for K_{1a} , K_{1b} , K_{1c} , and K_{1d} at the temperature range of 278K to 348K

and its calculated values are listed in **(Table 7)**. The branching ratio plot for rate constant associated with the formation of I1a, I1b, I1c and I1d are shown in **Figure 13**. Hence, the calculated total kinetic rate constant is used to calculate the atmospheric lifetime. The atmospheric lifetime of Cl-isoprene adduct radical can be calculated using the following given expression

$$\tau = \frac{1}{K [\text{Cl}]}$$

Where K is the total rate constant obtained from the above kinetic studies and Cl is the atmospheric concentration of the Cl atom. Under the atmospheric condition, the Cl concentration is 1×10^5 molecules per cm^3 ^[52]. The troposphere lifetime (τ) of isoprene is estimated from the total rate coefficient value of primary Cl-isoprene adduct radical reaction at the temperature range of 298K. The lifetime of Cl-isoprene adduct radical is estimated to be 6.49 hours at the temperature of 298K using the average atmospheric concentration of Cl atom. The lifetime reported in this study is in good agreement with the Gaia Fantechi et al estimated values of 5 hours^[53].

Energy and reaction force profiles

In Figure 14 & 15, the energy and reaction force profiles along with the partition of the reaction coordinates are shown. As stated by the transition state theory (TST), an energy profile of the all reaction path are characterized in three critical points such as two minimum points, one reactant (ξ_R) and another product (ξ_p), and one maximum point for the transition structure (ξ_{TS}). In the reaction force profile, the critical points are divided into three separate reaction regions that are reactants $\xi_R \rightarrow \xi_1, \xi_1 \rightarrow \xi_2$ and $\xi_2 \rightarrow \text{product}(\xi_p)$. The first region is the preparation region associated with the reactants (ξ_R, ξ_1), where the structural distortion takes place mainly by the bond stretching, angle bending, etc. In this region, when the negative (retarding) reaction force reaches its greatest strength at the point ξ_1 , the reaction force $F(\xi)$ becomes minimum. The second region is a transition state region which is located from ξ_1 to its maximum point at ξ_2 and where the structural rearrangements take place by the bond breaking and bond forming. All of these extensive changes produce a positive reaction force which starts at ξ_1 that gradually overcomes the retarding one. At the point ξ_{TS} , the positive deriving force is dominant and continues to increase until it reaches its maximum reaction force at ξ_2 where the system has been changed as the states of the products. Finally, the third region is the product region which is located from the $F(\xi)$ maximum at ξ_2 to its minimum point at ξ_p . In this region, the system involves structural relaxation to reach its final state after the maximum point at ξ_2 and the reaction force $F(\xi)$ declines to zero to reach the equilibrium geometry of the products.

On the other hand, reaction force calculation has been performed to estimate the amount of work done in each elementary step of the chemical reaction. The calculated work is done for the formation of Cl isoprene adduct radical intermediates I1a, I1b, I1c, and I1d are listed in supplementary **(Table S5)**. From the **(Table S5)**, the formation of Cl-isoprene adduct radical intermediates (I1a, I1b, I1c, and I1d), 70%, 77.5%, 74.1%, and 77.6% of activation energy is due to the geometrical rearrangement and the remaining 30%, 22.5%, 25.9%, and 22.4% of activation energy is due to electronic reordering respectively. In this mechanism, the potential end products P3 (MVK with CH_2O) and P4 (MACR with CH_2O) is formed through the addition of Cl, O_2 and NO radical pathway. During the formation P3, 71% & 29% of activation energies are mainly due to the geometrical rearrangement and electronic reordering respectively. Similarly, the formation of P4, 72% & 28% of activation energies were due to geometrical rearrangement and electronic reordering respectively. On the other hand, the potential end products P6 (MVK with H_2O_2) and P7 (MACR with H_2O_2) is formed through the addition of Cl, O_2 , and H_2O pathway. In the formation of P6 and P7, 75% & 76% of activation energies are due to geometrical rearrangement, the remaining 25% & 24% of activation energies are due to electronic reordering respectively listed in **(Table S6)**. This analysis shows that the potential product P3 and P4 are formed with less activation energy than the potential product of P6 and P7, which confirms that the formation of MVK and MACR through Cl, O_2 , and NO radical addition pathway is more favorable than the formation of MVK and MACR through Cl, O_2 , and H_2O addition pathway. The kinetic study also reveals that the formation of MVK and MACR via Cl, O_2 , and NO radical addition pathway is more favorable.

The relative energy profile also shows that the formation of MVK through Cl, O₂, and NO radical addition pathway has less activation energy than the formation of MVK through Cl, O₂, and H₂O addition pathway. Similarly, the formation of MACR through Cl, O₂, and NO radical addition pathway has less activation energy than the formation of MACR via Cl, O₂, and H₂O addition pathway. Thus the result shows that the H₂O molecule can affect the formation of SOAs such as MVK and MACR. All previous results are in good agreement with this reaction force analysis.

CONCLUSION

In this present work, the atmospheric reaction of isoprene initiated by chlorine atom at various channels and subsequent reactions by the addition of O₂ molecule, NO radical, and H₂O were investigated by using quantum chemical methods. The kinetics of the primary and subsequent reactions of isoprene were carried out by CVT/SCT. The electronic structure of reactant, transition state, intermediate complexes, intermediates, and products were optimized with M06-2X/6-311+G* level of theory and their corresponding single point energy was carried out by using CCSD (T)/6-311+G* level of theory. All reactants, intermediates, and products possess zero imaginary frequency and transition states possess a single imaginary frequency. All Transition States were confirmed through Intrinsic Reaction Coordinates (IRC) to identify the preferred reactants, intermediates and products. The conclusions of the brief explorations are summarized below,

1. The initial reaction of isoprene was studied by Cl radical addition at the various position with the C—C bond breaking which leads to the formation of secondary reaction and its bond length and bond angles were calculated from the optimized structure.
2. All the reaction paths are found to be exothermic and spontaneous with a maximum energy barrier. Whereas the potential end product (MVK, MACR) through Cl, O₂, and NO radical addition pathway is found to be more spontaneous and feasible compared to the formation of the end product (MVK, MACR) through Cl, O₂, and H₂O addition pathway. The calculated $\Delta H = -0.129$ kcal/mol (MVK through Cl, O₂, and NO) $> \Delta H = 6.219$ kcal/mol (MVK through Cl, O₂, and H₂O) and $\Delta G = -5.479$ kcal/mol (MACR through Cl, O₂, and NO) $> \Delta G = 2.369$ kcal/mol (MACR through Cl, O₂, and H₂O).
3. The most favorable active site of isoprene is found to be at terminal C4 and C5 position with its corresponding value is 0.289 and 0.099 by using Condensed Fukui Function analysis and also it elucidates the concept of bond breaking and bond forming.
4. The calculated rate constants for the reaction between isoprene and Cl radical is found to be 4.89×10^{-11} , 6.91×10^{-10} , 1.63×10^{-10} and 8.12×10^{-10} cm³/molecule/sec respectively at 278K and it is compared with the experimental rate coefficient of 4.6×10^{-10} at 298K. The lifetime of Cl-isoprene adduct radical is estimated to be 6.49 hours at the temperature of 298K using the average atmospheric concentration of Cl atom
5. The reaction force analysis reveals that the geometrical rearrangement of each structure plays a major part than electronic reordering. The formation of Cl-isoprene adduct radical intermediates (IIa, IIb, IIc, and IId), 70%, 77.5%, 74.1%, and 77.6% of activation energy is due to the geometrical rearrangement and the remaining 30%, 22.5%, 25.9%, and 22.4% of activation energy is due to electronic reordering respectively.
6. Conclusively, the kinetic and thermodynamic results reveal that the electrophilic addition of Cl radical to the terminal carbon atom plays the dominant role in the marine boundary and H₂O molecule can affect the formation of SOAs such as MVK and MACR. The calculated lifetime in this work reveals that the isoprene degrade quickly in the atmosphere.

Conflicts of interest

No conflicts to declare

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