# *Original Research Article*

# Unveiling the Atmospheric Oxidation of E2CAA initiated by Cl Radical: DFT Study

**ABSTRACT**

Ethyl 2-chloroacetoacetate (CH₃C(O)CHClC(O)OCH2CH₃, E2CAA) is a class of volatile organic compound which finds their place in atmosphere by anthropogenic sources. However, its extensive presence in industrial processes raises concerns about its environmental impact. The present study focused on investigation of atmospheric oxidation of E2CAA initiated by Cl atom. The fate of these E2CAA is however poorly understood and scarcely taken into account in atmospheric chemistry modeling. The objective of this study is to unravel the reaction mechanism, thermodynamics, and kinetics by means of theoretical method. A comprehensive theoretical investigation was conducted to elucidate the mechanism, kinetics, and thermochemistry of the gas-phase reactions between E2CAA and Chlorine radical using the M06-2X functional. The most thermodynamically stable conformer of E2CAA was identified at ambient temperature. Four primary hydrogen abstraction pathways were characterized, each proceeding through the formation of a pre-reactive complex, indicating that the reactions follow an indirect hydrogen abstraction mechanism. Rate coefficients for these pathways were calculated for the first time over a temperature range of 250–450 K using Canonical Transition State Theory (CTST). Based on these kinetic results, the atmospheric lifetime of E2CAA was estimated to be approximately 2.68 days.

**Keywords:** Ester, chloroacetoacetate, DFT, IRC calculation, Rate constant

1. **Introduction**

In recent decades, it has been stated that volatile organic compounds (VOCs), most likely hydrofluoroethers (HFEs), are widely acknowledged and recommended as a third-generation alternative to hydrofluorocarbons (HFCs), hydrochlorofluorocarbons (HCFCs), and chlorofluorocarbons (CFCs). These substances are used in refrigerator heat transfer fluid, foam blowing agents, lubricant deposition, and electronic equipment cleaning (Devotta et al., 1994., sekiya and Misaki., 2000, Powell., 2002). The primary mechanisms for HFE degradation in the atmosphere may be initiated in coastal locations by reactions with OH radicals and Cl atoms, as well as possibly with aerosols containing chloride from highly mechanized metropolitan areas.

Solvents, fuel additives, and cleaning and disinfection chemicals are all made with oxygenated volatile organic compounds, (OVOCs.) These substances can primarily undergo chemical transformations when released into the atmosphere, producing reaction products that may be more dangerous than the precursors (Zhou et al., 2006; Christensen et al., 2000). OH radical-initiated photo oxidation processes are the primary pathway for OVOC oxidation in the troposphere (Han et al., 2018; Bouzidi et al., 2015). The family of Oxygenated Volatile Organic Compounds (OVOCs) known as carbonyl esters includes methyl 2-chloroacetoacetate (M2CAA) and ethyl 2-chloroacetoacetate (E2CAA) (DeMore et al., 1997). These VOCs have an oxygen bond that increases the reactivity of the molecule's neighboring hydrogen atoms to tropospheric oxidants like photolysis or OH or Cl radicals. Acetates have been widely released into the atmosphere as a result of industrial activity; these oxygenated volatile organic compounds will react with the primary tropospheric oxidants (Blanco et al., 2016; Bravo et al., 2011).

Chemical transformation is the primary determinant of these chemicals' destiny in the atmosphere. The primary cleaner in the marine boundary layer, chlorine atoms are crucial to the breakdown of OVOCs-initiated photo oxidation processes, which are brought on by the addition of a double bond or by mechanisms of hydrogen atom abstraction (Atkinson et al., 1997). Similarly, larger concentrations of Cl atoms, which can reach 1×105 atoms cm−3 or more, in marine or heavily industrialized (Blanco et al., 2012) environments may result in competitive interactions with the OH radical that triggered the breakdown of these VOCs (Blanco et al., 2009).

Certain OVOCs, such as chloroacetoacetates, which are commonly employed as anti-slime antimicrobial and pesticide agents to eradicate slime-producing microorganisms such algae, fungi, and slime molds on pools, are released by the paper industry. These substances can be transmitted to water reservoirs or evaporate into the atmosphere if they are often used as insecticides. Instead of dry and wet deposition, chemical transformation is the primary determinant of the sink of OVOCs, such as esters and haloesteres. Methyl 2-chloroacetoacetate was used in one-pot synthesis of 2-arylimidazole-4-carboxylic acids and 3,5-disubstituted 1,2,4-triazoles (Yoburn and Baskaran, 2005; Tseng et al., 2011). To ascertain their environmental impact on the quality of air and other matrices, kinetic and mechanistic analyses of the degradation of chloroacetoacetates triggered by interaction with Cl radicals are pertinent. A well-defined theoretical study is very desirable in order to identify the feasible mechanism and gain a better grasp of the kinetics of the title reaction. In order to gain a more thorough knowledge of the title reaction, we presented a thorough theoretical analysis of the hydrogen abstraction reaction between E2CAA and Cl radical as an addition to the experiments.



However, there has only been one experimental research project on kinetic of E2CAA + Cl reaction as far as we know. Recently, Straccia et al., (2023) reported the Rate coefficients for the gas-phase reactions of Cl radical with E2CAA using the relative technique with different reference compounds. They reported a rate constant value as (2.41 ± 0.57) ×10-10 cm3 molecule−1 s−1at (298 ± 2) K. It has been also reported that by employing structure activity relationship (SAR) method, Aschmann and Atkinson, (1995) estimated rate coefficients for the reactions of E2CAA with Cl atoms. The SAR value for the reaction of E2CAA with chlorine atoms is established to be 8.29×10-11 cm3 molecule−1 s−1. As far as we are aware, this is the first thorough theoretical investigation of E2CAA's H-abstraction interactions with Cl radical. We think that our work will be helpful for a better understanding of this significant reaction, since experimental study mainly provides just the overall rate constant.



**2. COMPUTATIONAL METHODS**

We performed all the computational quantum calculations work using Gaussian 09 program package (Frisch et al., 2009). The electronic structures of the reactants (Rs), reaction complexes (RCs), product complexes (PCs), transition states (TSs) and products (Ps) were optimized using hybrid density functional M06-2X (Zhao and Truhlar, 2008) along with 6-31+G(d,p) basis set. Further, we were carried out frequency calculations of all the optimized species using the same M06-2X /6-31+G(d,p) method. From frequency analysis, we found that for stable species, these were no imaginary frequencies which ensure these molecules to have either local or global minima energies while for the TSs, we found one imaginary frequency to ensure it has maxima along the reaction coordinate. Previous reports (Gour et al., 2020; Lily et al., 2014; Rao et al., 2018; Baidya et al., 2020; Paul et al., 2020; Gour et al., 2017) have demonstrated that this hybrid density functional, M06-2X, produces satisfactory results for thermochemistry and kinetics for the hydrogen abstraction reactions for the volatile organic compounds. In order to validate to correct TSs which was really connecting the reactant and product species, we performed IRC calculation (Gonzalez and Schegel, 1989) throughout the reaction channels.

**3. RESULTS AND DISCUSSION**

We first identified the most stable E2CAA conformers using scan calculations, and we then chose the most stable conformer for further study. For the hydrogen abstraction reactions, we have considered four reaction routes (1-4), mainly hydrogen abstraction from the −CH3 group, −CHCl group, and −COOCH2 and −COOCH2CH3 group. For the reaction channels (1-4), we have located four transition states viz., TS1, TS2, TS3 and TS4, respectively on the relaxed potential energy surface. Pre-reactive complexes (RC1, RC2, RC3 and RC4) have been found in the entrance channel for reactions (1-4) in the current investigation. The exit channel also contains product complexes, referred to as PC1, PC2, PC3 and PC4, with energies lower than the corresponding products before the final product is distributed. Therefore, it is clear that the reaction channels (1-4) may employ indirect procedures. The least energy path was used to find stationary spots on a relaxed potential energy surface. Figs. 1 and 2 show the electronic structure of the optimized geometry of the reactant, products, reaction complexes, product complexes, and transition states that were produced at the M06-2X/6-31+G(d,p) level.

At the M06-2X/6-31+G(d,p) level, the precise thermodynamic calculations for reaction enthalpies (ΔrH°) and free energies (ΔrG°) at 298 K for loss processes (1−4) are documented in Table 1. These thermodynamic functions were determined with thermal corrections to the energy at 298 K. The calculated ΔrH° and ΔrG° values at 298 K indicate that the decomposition pathways taken into consideration in this investigation are feasible and spontaneous. It is evident from Table 1 that the reaction channels (1-3) are exothermic and exergonic in nature. However, reaction channel 4 is found to be endothermic and endogenic in nature.

The C−H bond of the departing hydrogen and the newly generated bond between the H and Cl atom are crucial structural characteristics that must be monitored throughout the development of transition states. The breaking C−H bond length is 26.71% greater than the observed C−H bond length in the isolated E2CAA molecule, while the forming H...Cl bond length is 16.95% longer than the H−Cl bond length in isolated HCl molecule, according to a visualization of the optimized structures of TS1 for reaction 1. This implies that the barrier of the reaction 1 is closer to the product. It is emphasized that the reactions with Cl atoms proceed via late transition state which is in consonance with Hammond’s postulate (Hammond, 1995). Similarly, for transition state TS2 for reaction 2, the length of the breaking C−H bond (C13-H10) is found to be longer by 15.59% than the observed C-H bond length in isolated E2CAA molecule whereas the forming H...Cl bond length is longer by 24.06% than the H−Cl bond length in isolated HCl molecule. This implies that the barrier of the reaction 2 is closer to the reactant, and that the reactions with Cl atoms proceed via early transition state. Visualization of the optimized structures of TS3 for reaction 3 reveals that the length of the broken C-H bond (C3 −H5) is 24.95% longer than the C−H bond length that was determined in the isolated E2CAA molecule whereas the forming H...Cl bond length is elongated from 1.280 Å to 1.487 Å (16.17%) than the H-Cl bond length in isolated HCl molecule. Similar, observation of the electronic structure as depicted in Fig. 1 suggests that broken C−H bond (C15 −H16) is 35.86% longer than the C−H bond length that was determined in the isolated E2CAA molecule whereas the forming H...Cl bond length is elongated from 1.280 Å to 1.416 Å (10.62%) than the H-Cl bond length in isolated HCl molecule.

Table 2 presents the results of the harmonic vibrational frequency calculation at the M06-2X/6-31+G(d,p) level. Each transition state has one imaginary frequency due to its first order saddle point character, while the analysis of the harmonic vibrational frequency of minima including reactants, reactant complexes (RCs), product complexes (PCs), and products (P1 and P2) revealed no imaginary frequency (NIMAG = 0). The C6–H19 and Cl20–H19 stretching modes are represented by the imaginary frequency of TS1 for reaction channel (1), which is 1211 cm−1. This also shows a considerable curvature in the potential energy surface (PES) surrounding the transition state.‬ The imaginary frequency for the hydrogen abstraction from the −CHCl group involving TS2 is determined to be 480 cm

The representation of the normal-mode corresponding to the calculated imaginary frequencies shows a clear transition state geometry connecting reactants and products during transition. To further ascertain whether a transition state exists on the potential energy surface, the intrinsic reaction coordinate (IRC) calculation (Gonzalez and Schegel, 1989) is performed at the same theoretical level using the Gonzalez-Schlegel steepest descent path in the mass-weighted Cartesian coordinates with a step size of 0.01(amu1/2- bohr). Additional proof that the transition state truly connects the intended reactant and product along the corresponding potential energy surface is given by the results of IRC calculations, which are shown in Fig. 3. Table 3 summarizes the energy of each optimized geometry used in this study, which was determined using the M06-2X/6-311++G(d,p) method. We employed the species' optimal geometries, M06-2X/6-31+G(d,p), for the energetic computation. Using frequency calculation data at the M06-2X/6-31+G(d,p) level of theory, optimization was carried out to find each species' zero-point energy. Zero-point energy (ZPE) corrected total energies were calculated with a scale factor of 0.967 (Alecu et al., 2010). Fig. 4 shows a schematic potential energy profile of E2CAA reactivity with the Cl radical that was acquired at the M06-2X level using zero-point energy (ZPE) adjustments. Zero-point energy corrected total energy has been used in the energy diagram's development. The ground state energy of E2CAA + Cl, which includes ZPE, is plotted against these energies, with zero being used randomly. For TS1, TS2, TS3 and TS5, the energy barrier determined at the M06-2X/6-31+G(d,p) level is 2.65, −1.79, −3.62 and 2.59 kcal mol−1, respectively.

**3.1 KINETICS CALCULATION**

The conventional transition state theory (CTST) (Laidler, 2004) and Eckart's tunneling correction (Xiao et al., 2014) were used to calculate the rate coefficient values for various reaction channels spanning the 250–450 K temperature range using the following formula.



The σ represents symmetry factor whereas tunneling correction factor at temperature T is represented by the symbol Γ(T). The total partition functions (per unit volume) for the reactants and transition states are denoted by QR and ,, respectively. R stands for the universal gas constant, kB for the Boltzmann constant, h for Planck's constant, and ΔE for the barrier height incorporating zero point energy correction. In present work, the kinetic rate coefficients for reaction pathways (1−3) were performed by means of the Kinetic and Statistical Thermodynamical Package (KiSThelP) programme (Canneaux et al., 2014). The obtained rate coefficients in the temperature range of 250 – 450 K for reaction pathways (1–4) are recorded in Table 4. At 298 K, our calculated rate constants for TS1, TS2, TS3 and TS4 were found to be 2.83×10−14 , 4.47×10−11, 3.86×10−10 and 2.43×10−13 cm3 molecule−1 s-1 respectively at M06-2X/6-31+G(d,p) level of theory. The computed overall kCl value for E2CAA with Cl atom reaction using the M06-2X barrier height is found to be 4.32×10-10 cm3 molecule-1 s-1 at 298 K. Our calculated rate constant for the reaction of E2CAA with Cl atom is in good agreement with the reported value of (2.41 ± 0.57) ×10-10 cm3 molecule-1 s-1 at (298 ± 2) K by Straccia et al., (2023). The percentage branching ratios for each of the reaction channels determined at 298 K clearly indicates that 89.58 % of hydrogen abstraction proceeds from –COOCH2 group. From these results, it can be emphasize that the hydrogen abstraction from the −COOCH2 group is kinetically more advantageous than the other three reaction pathways i.e. abstraction from –CH3 –CHCl and –COOCH2CH3 group.



**3.2 ATMOSPHERIC LIFETIME**

In general, tropospheric lifetime (τeff) of E2CAA can be estimated by assuming that its removal from troposphere occurs only through the reactions with Cl atoms. Then (τeff) can be expressed as (Kurylo and Orkin, 2003),

τeff = τCl(4)

where, τCl = (kCl × [Cl])-1. Using the 298 K value of kCl = 4.32×10−10 cm3 molecule−1 s−1 and the global average atmospheric Cl concentrations of 1.0 ×104 molecule cm−3 (Wingenter et al., 1996), the estimated atmospheric lifetime of E2CAA is found to be 2.68 days which is in good agreement with the reported value of 4.6 days by Straccia et al., (2023).

**4. CONCLUSIONS**

In this study we have explored the atmospheric and environmental consequence of E2CAA molecule initiated by Cl radical by employing M06-2X/6-31+G(d,p) level of theory. We have done various inquires involving the optimization of structural parameters, energy profiles, thermochemistry, and kinetics of the Cl atom initiated degradation of E2CAA. For that, we have identified four reaction channels which follow an indirect path through the formation of pre- and post- reaction complexes on the potential energy surface. In this manuscript, we applied an effective as well as reliable computational strategy for predicting accurately the tropospheric reactivity of the titled molecule and atmospheric implications. All rate constants, computed by canonical transition state theory are in reasonable agreement with the limited experimental data. The thermal rate constant for the H atom abstraction of E2CAA by Cl radicals is found to be 4.32×10−10 cm3 molecule−1 s−1 at 298 K which aligns closely with the experimental rate. The atmospheric lifetime for E2CAA molecule is estimated to be 2.68 days. From our theoretical study along with experimental evidence it can be concluded that hydrogen abstraction from –COOCH2 group is more facile in atmospheric condition.

**DISCLAIMER (ARTIFICIAL INTELLIGENCE)**

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc.) and text-to-image generators have been used during the writing or editing of this manuscript.

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**Table 1** Thermochemical data (kcal mol−1.) for reaction channels (1−4) calculated at M06-2X/6-31+G(d,p) level of theory at 298 K.

|  |  |  |
| --- | --- | --- |
| Reaction channels | **ΔrH°298** | **ΔrG°298** |
| Reaction 1 | −3.88 | −5.24 |
| Reaction 2 | −9.45 | −11.58 |
| Reaction 3 | −2.24 | −5.26 |
| Reaction 4 | 3.13 | 0.72 |

**Table 2** Harmonic vibrational frequencies of reactants, transition states and products at M06-2X/6-31+G(d,p) level of theory.

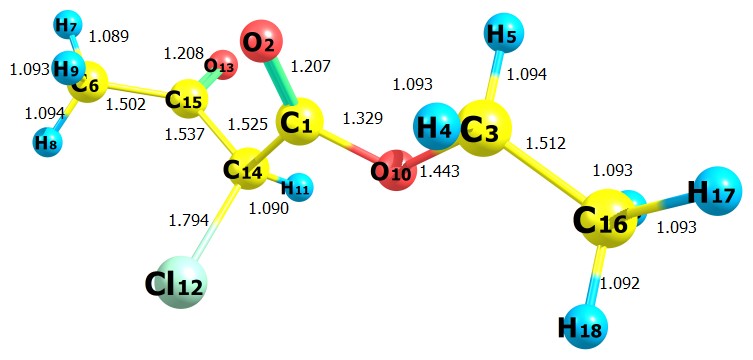
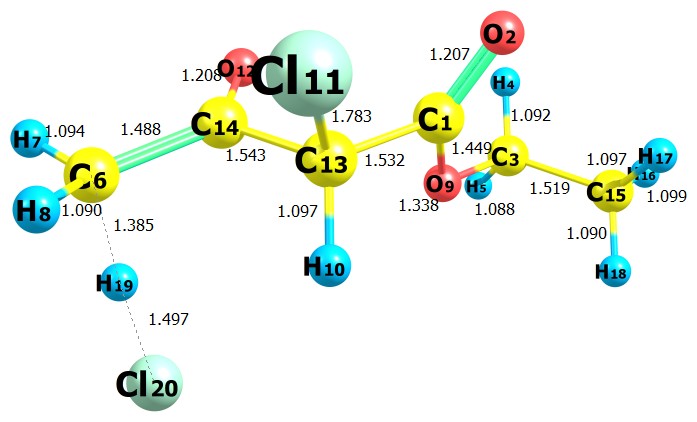
|  |  |
| --- | --- |
| **Species** | **Vibrational Frequencies (cm-1)** |
| CH3C(O)CHClC(O)OCH2CH3  (E2CAA) | 28, 58, 68, 112, 133, 160, 178, 228, 231, 311, 337, 393, 462, 506, 574, 675, 758, 799, 815, 891, 918, 963, 1023, 1038, 1088, 1128, 1180, 1201, 1226, 1279, 1334, 1363, 1404, 1407, 1437, 1472, 1483, 1493, 1504, 1515, 1868, 1893, 3072, 3080, 3119, 3136, 3151, 3157, 3164, 3186, 3192 |
| TS1 | 1211i, 33, 48, 64, 71, 90, 122, 154, 190, 212, 255, 312, 331, 380, 418, 463, 483, 550, 589, 670, 760, 800, 811, 868, 905, 917, 954, 1000, 1026, 1076, 1124, 1148, 1176, 1197, 1225, 1294, 1330, 1357, 1403, 1432, 1451, 1492, 1502, 1516, 1818, 1852, 3051, 3110, 3120, 3126, 3131, 3165, 3200, 3241, |
| TS2 | 480i, 22, 42, 60, 82, 90, 100, 131, 148, 194, 222, 245, 312, 325, 369, 399, 464, 541, 566, 657, 769, 818, 837, 890, 932, 965, 993, 1034, 1054, 1088, 1122, 1139, 1206, 1230, 1311, 1346, 1402, 1404, 1436, 1467, 1475, 1495, 1510, 1520, 1871, 1881, 3075, 3081, 3121, 3154, 3162, 3172, 3194, 3196, |
| TS3 | 858i, 12, 25, 33, 63, 111, 129, 132, 142, 175, 206, 254, 261, 321, 385, 407, 486, 500, 565, 669, 770, 795, 803, 905, 921, 966, 997, 1029, 1035, 1046, 1158, 1164, 1191, 1217, 1220, 1266, 1340, 1384, 1399, 1435, 1470, 1476, 1481, 1487, 1876, 1921, 3058, 3080, 3123, 3143, 3156, 3170, 3182, 3196 |
| TS4 | 668i, 18, 21, 37, 73, 82, 107, 128, 160, 197, 229, 299, 318, 369, 386, 458, 500, 573, 638, 678, 759, 773, 795, 816, 844, 904, 937, 1003, 1032, 1055, 1082, 1172, 1191, 1204, 1224, 1272, 1330, 1350, 1402, 1415, 1467, 1477, 1479, 1504, 1866, 1896, 3078, 3126, 3127, 3154, 3156, 3190, 3193, 3264 |
| RC1 | 15, 27, 49, 59, 65, 81, 112, 126, 161, 178, 222, 235, 310, 335, 391, 461, 507, 574, 673, 757, 797, 815, 889, 918, 962, 1020, 1034, 1086, 1128, 1176, 1200, 1222, 1278, 1331, 1358, 1397, 1404, 1435, 1470, 1475, 1496, 1504, 1515, 1870, 1895, 3074, 3077, 3110, 3116, 3154, 3156, 3162, 3182, 3190 |
| RC2 | 18, 35, 54, 57, 72, 92, 103, 136, 159, 188, 216, 249, 312, 332, 378, 465, 533, 565, 661, 761, 808, 817, 887, 921, 956, 1012, 1040, 1084, 1127, 1181, 1200, 1219, 1288, 1337, 1353, 1398, 1405, 1437, 1471, 1478, 1497, 1502, 1516, 1873, 1903, 3075, 3077, 3121, 3135, 3154, 3157, 3170, 3190, 3194 |
| RC3 | 16, 30, 56, 67, 86, 92, 102, 119, 130, 188, 217, 246, 276, 337, 403, 419, 511, 569, 695, 765, 798, 811, 894, 914, 974, 1018, 1046, 1088, 1152, 1184, 1221, 1256, 1278, 1307, 1366, 1394, 1410, 1449, 1460, 1468, 1497, 1507, 1523, 1825, 1858, 3074, 3083, 3101, 3150, 3154, 3166, 3175, 3201 |
| RC4 | 22, 30, 48, 67, 73, 94, 136, 141, 171, 196, 228, 273, 310, 344, 395, 460, 501, 570, 682, 759, 796, 813, 892, 920, 962, 1023, 1037, 1088, 1127, 1181, 1199, 1226, 1275, 1334, 1360, 1399, 1402, 1438, 1471, 1478, 1495, 1504, 1517, 1866, 1894, 3061, 3080, 3121, 3131, 3135, 3154, 3162, 3187, 3203 |
| PC1 | 15, 28, 53, 67, 74, 100, 112, 153, 181, 228, 247, 314, 350, 411, 429, 455, 507, 518, 533, 589, 687, 768, 807, 835, 852, 895, 932, 974, 1033, 1080, 1127, 1198, 1227, 1258, 1304, 1329, 1353, 1401, 1433, 1492, 1493, 1505, 1515, 1650, 1877, 2697, 3073, 3116, 3155, 3160, 3161, 3186, 3218, 3341, |
| PC2 | 26, 47, 70, 89, 94, 111, 120, 177, 178, 222, 250, 258, 326, 354, 386, 409, 445, 483, 527, 564, 611, 746, 780, 831, 893, 970, 1029, 1035, 1054, 1121, 1136, 1203, 1303, 1320, 1344, 1401, 1404, 1434, 1470, 1480, 1494, 1502, 1512, 1741, 1817, 2765, 3074, 3079, 3121, 3152, 3156, 3168, 3194, 3201 |
| PC3 | 12, 30, 58, 79, 96, 107, 136, 139, 164, 165, 213, 247, 264, 331, 338, 377, 388, 404, 452, 491, 569, 686, 777, 790, 902, 923, 983, 1010, 1033, 1041, 1158, 1167, 1200, 1232, 1279, 1349, 1386, 1404, 1445, 1468, 1472, 1477, 1491, 1853, 1892, 2842, 3020, 3081, 3105, 3127, 3156, 3161, 3202, 3300 |
| PC4 | 15, 24, 38, 53, 76, 78, 118, 163, 171, 194, 206, 238, 308, 312, 315, 380, 392, 459, 502, 570, 680, 686, 762, 795, 820, 910, 930, 992, 1033, 1048, 1096, 1176, 1189, 1218, 1275, 1325, 1347, 1403, 1410, 1471, 1474, 1482, 1504, 1869, 1894, 2812, 3085, 3119, 3126, 3163, 3183, 3187, 3199, 3306 |
| CH2C(O)CHClC(O)OCH2CH3 (P1) | 33, 61, 95, 98, 141, 192, 224, 261, 292, 329, 375, 428, 438, 517, 583, 684, 770, 794, 817, 845, 903, 922, 994, 1033, 1094, 1152, 1184, 1198, 1229, 1305, 1314, 1362, 1405, 1445, 1476, 1498, 1507, 1522, 1668, 1898, 3083, 3099, 3142, 3146, 3168, 3172, 3202, 3323 |
| CH3C(O)CClC(O)O CH2CH3 (P2) | 30, 58, 83, 99, 119, 162, 202, 236, 261, 273, 330, 389, 438, 468, 565, 578, 743, 804, 812, 899, 972, 1028, 1033, 1081, 1128, 1153, 1184, 1292, 1307, 1337, 1403, 1407, 1446, 1473, 1485, 1496, 1506, 1525, 1745, 1838, 3077, 3079, 3095, 3141, 3151, 3166, 3168, 3195 |
| CH3C(O)CHClC(O)O CHCH3 (P3) | 15, 64, 79, 94, 124, 138, 172, 187, 234, 261, 343, 394, 410, 468, 534, 558, 692, 762, 801, 889, 912, 985, 1006, 1026, 1059, 1160, 1175, 1230, 1251, 1263, 1354, 1388, 1405, 1446, 1472, 1473, 1481, 1492, 1854, 1873, 3024, 3079, 3101, 3159, 3161, 3175, 3196, 3294 |
| CH3C(O)CHClC(O)O CH2CH2 (P4) | 28, 67, 90, 110, 132, 141, 159, 188, 230, 252, 336, 393, 411, 529, 553, 600, 706, 759, 802, 820, 893, 958, 982, 1027, 1058, 1124, 1176, 1221, 1252, 1260, 1300, 1356, 1401, 1414, 1470, 1479, 1492, 1518, 1851, 1873, 3080, 3110, 3158, 3165, 3181, 3198, 3209, 3323 |
| HCl | 3033 |

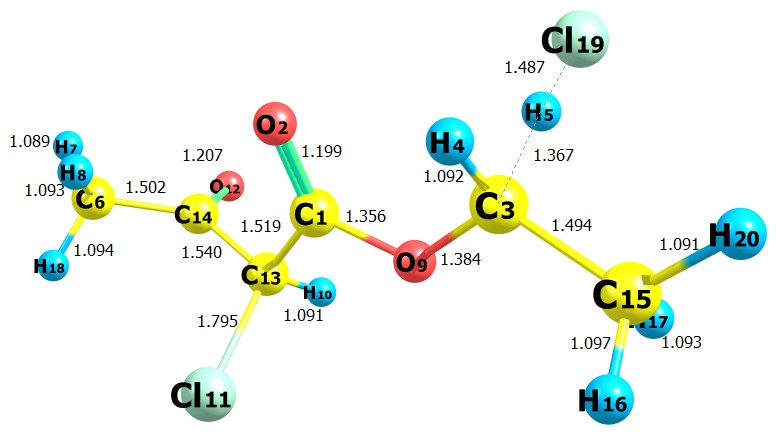
**Table 3** Relative energies (in kcal mol−1) with zero-point energy correction for the reactants, reaction complexes, transition states, product complexes and products at M06-2X/6-31+G(d,p) level of theory.

|  |  |
| --- | --- |
| **Species** | **M06-2X/6-31+G(d,p)** |
| E2CAA+ Cl | 0.00 |
| RC1 | 0.03 |
| RC2 | −4.28 |
| RC3 | −6.87 |
| RC4 | −0.45 |
| TS1 | 2.65 |
| TS2 | −1.79 |
| TS3 | −3.62 |
| TS4 | 2.59 |
| PC1 | −10.38 |
| PC2 | −18.12 |
| PC3 | −7.84 |
| PC4 | 0.74 |
| P1 + HCl | −4.05 |
| P2 + HCl | −9.88 |
| P3 + HCl | −2.88 |
| P4 + HCl | 2.56 |

**Table 4:** Rate constants of different reaction channels and overall rate constant (in cm3 molecule−1 s−1) within the temperature range of 250−450 K at M06-2X/6-31+G(d,p) level of theory.

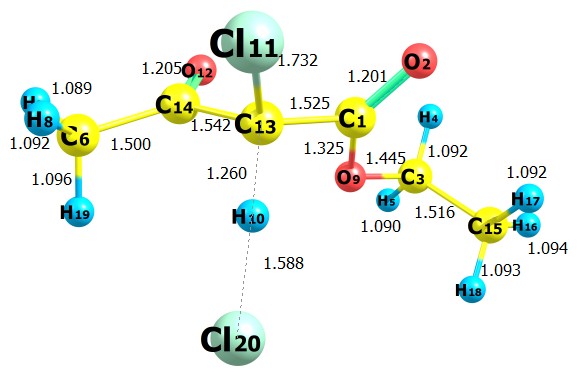
|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Rate constant** | **250 K** | **298.15 K** | **300 K** | **350 K** | **400 K** | **450 K** |
| k1 | 1.00 ×10−14 | 2.83×10−14 | 2.93×10−14 | 6.45×10−14 | 1.19×10−13 | 1.94×10−13 |
| k2 | 6.71×10−11 | 4.47×10−11 | 4.41×10−11 | 3.35×10−11 | 2.77×10−11 | 2.43×10−11 |
| k3 | 1.05×10−09 | 3.86×10−10 | 3.74×10−10 | 1.87×10−10 | 1.09×10−10 | 7.42×10−11 |
| k4 | 8.79 ×10−14 | 2.43 ×10−13 | 2.51 ×10−13 | 5.46 ×10−13 | 9.94 ×10−13 | 1.60×10−12 |
| Ktotal | 1.12×10−09 | **4.32×10−10** | 4.19×10−10 | 2.18×10−10 | 1.38×10−10 | 1.00×10−10 |





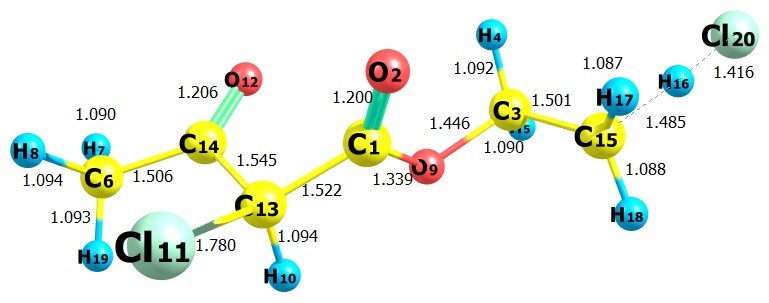
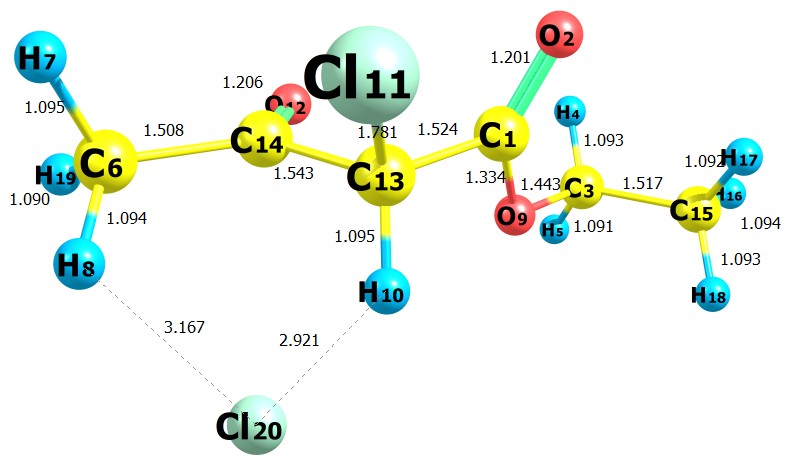
**TS1**

**E2CAA**



**TS3**

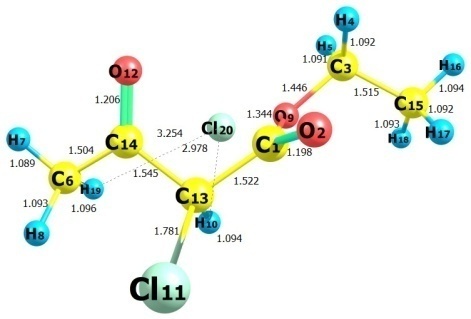
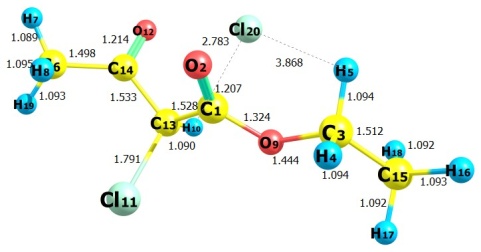
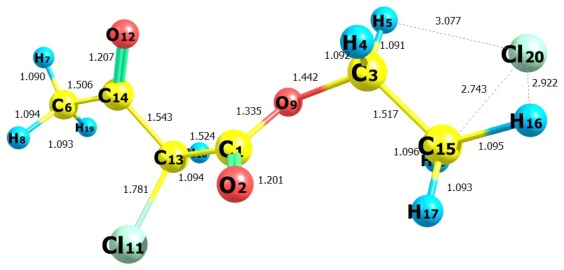
**TS2**



**RC1**

**TS4**

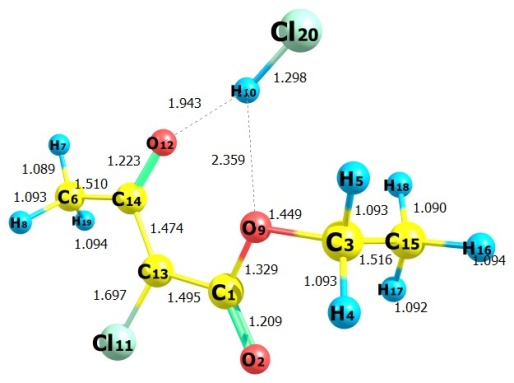
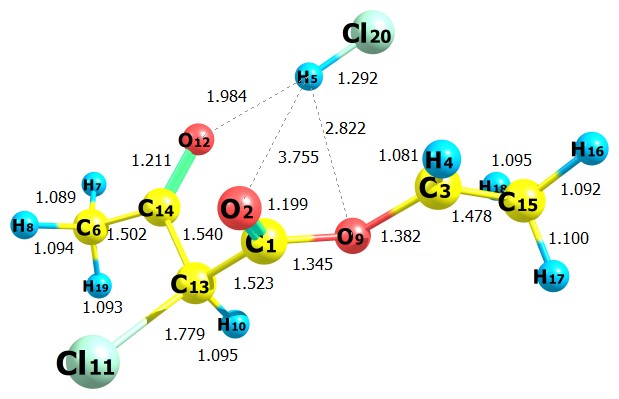
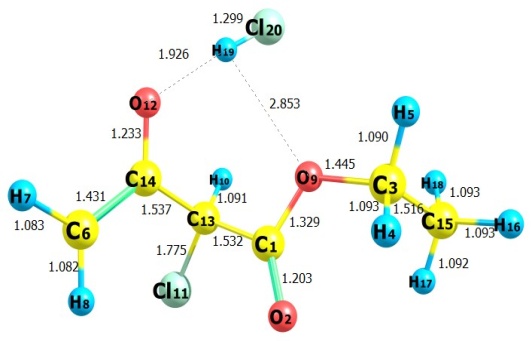
**Fig. 1:** Optimized geometries of E2CAA, transition states and reactive complexes at M06-2X/6-31+G(d,p)level.Bond lengths are in Angstroms.



**RC4**

**RC3**

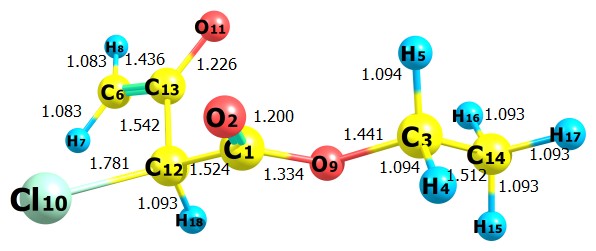
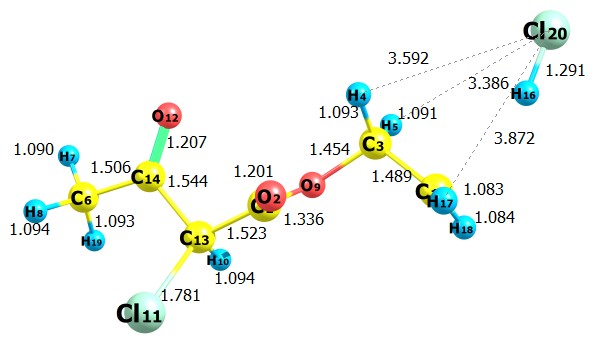
**RC2**



**PC3**

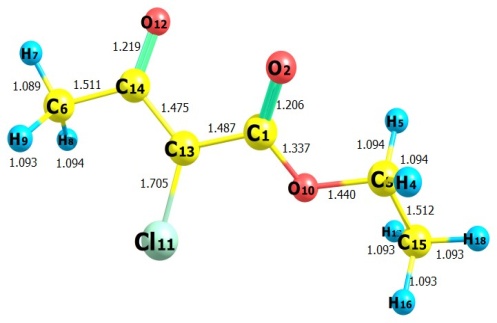
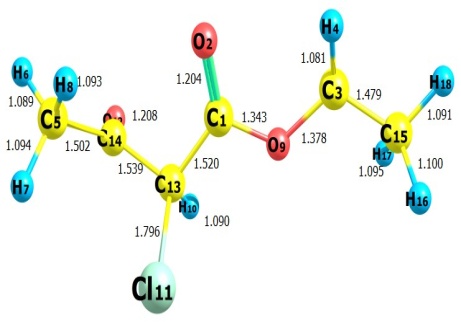
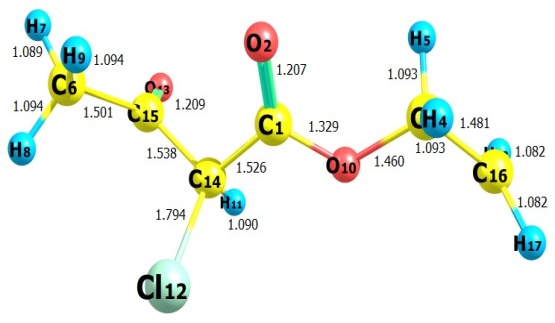
**PC1**

**PC2**



**P1**

**PC4**



**P4**

**P3**

**P2**

**PC2**

**Fig. 2:** Optimized geometries of product complexes and products at M06-2X/6-31+G(d,p) level.Bond lengths are in Angstroms.



**Fig. 3:** IRC plot performed for transition states TS1, TS2, TS3 and TS4 for reaction channels

(1-4) at M06-2X/6-31+G(d,p) level of theory.



**Fig. 4:** Schematic potential energy diagram for the E2CAA + Cl reactions. Relative energies (in kcal mol−1) with ZPE at M06-2X/6-31+G(d,p) level.