

Carbonyl Oxide Chemistry in Water Cluster: An Extended Computational Study

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Abstract

An extended computational approach has been utilized to explore the reactions of acids with carbonyl oxide, also known as Criegee intermediate (CI). The reactions were explored inside water cluster containing 50 water molecules. All possibilities of product formation were considered. Among the considered acids, the rate of 1,4-insertion follows the order - HCOO < HCl < HNO₃. The most stable products of the reactions between the considered acids and CI have been identified.

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ABSTRACT

An extended computational approach has been utilized to explore the reactions of acids with carbonyl oxide, also known as Criegee intermediate (CI). The reactions were explored inside water cluster containing 50 water molecules. All possibilities of product formation were considered. Among the considered acids, the rate of 1,4-insertion follows the order - HCOO < HCl < HNO₃. The most stable products of the reactions between the considered acids and CI have been identified.

1. Introduction: In atmosphere, ozone molecule occurs as open shell singlet di-radical. Ozone easily attack the double bond containing compounds and oxidized them by attacking at double bonded positions, which generates a highly reactive Criegee intermediate (CI), also known as carbonyl oxide.¹⁻⁴ It is found that tropospheric alkenes are the most significant source of Criegee intermediates.⁵⁻⁷ The general mechanism of alkene ozonolysis is shown below⁸⁻⁹ –

These produced CIs are found to have excess internal energy to undergo unimolecular processes, generally. But with acids, these CIs undergo bimolecular reaction so efficiently.¹⁰⁻¹² Studies found that some acids like HCl, H₂SO₄, HNO₃, HCOOH etc. are embedded on the surface of stratospheric region condensing with H₂O, they are also known as polar stratospheric particles, play a major role in scavenging CIs. During these scavenging reaction with acids, atmospheric H₂O budget are remarkably influenced.¹³

Early experimental data showed fast reactions of CI with formic acid (rate constant, $k_{\text{HCOOH}} = 1.1 \times 10^{-11} \text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$), hydrochloric acid (rate constant, $k_{\text{HCl}} = 4.0 \times 10^{-11} \text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$) and nitric

acid ($k_{\text{HNO}_3} = 5.4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).¹⁴⁻¹⁸ Their reaction rates are suggested with the help of their reaction rate co-efficient values.¹⁸⁻²⁰ The obtained high rate co-efficient values suggested that acids play a key role in scavenging CI in the atmosphere leading to the formation of low-volatile but highly oxidized molecules.²¹⁻²⁴ The obtained experimental data were also in agreement with theoretical values.¹³ Vereecken performed quantum chemical calculation to find out the probable barrierless pathways of these CI-acid reactions in gaseous phase.¹³ As it has been already discovered that water plays a significant role in atmospheric and environmental processes,²³⁻²⁸ so here in our study, all the possible pathways of the CI-acid reactions are studied in water cluster containing 50 water molecules using high level computational chemistry approach. Francisco *et. al.* have shown that the reaction of CI with nitric acid is greatly influenced by air-water interface.^{29a} Moreover, Lin *et. al.* have shown that the reaction of CI with alcohol is greatly enhanced by single water molecule.^{29b} However, to the best of our knowledge, no such study is available where the reaction between CI and acids are considered inside the water cage. The choice of 50 water cluster is due to the fact that it provides a full cavity (volume 166.3 \AA^3) where the reactions of CI and acids can be studied. Although the reaction of CI with acids have been studied in gas phase¹³ and in air-water interface,^{29a} the study of these reactions inside water cavity is also very essential for better understanding the fate of CI in aqueous environment.

2. Computational details: The water cluster containing 50 molecules of water was energy minimized using TIP4P model for water by using leap module of AMBER18 package. Steepest descent method was used for energy minimization and conjugate gradient method to discard any unfavourable interactions. The energy minimized water cluster was used for all other *abinitio* calculations. The gradient and hessian calculations were performed using M06-2X/6-311+G* level of theory.³⁰ We have used two layer ONIOM³¹ calculations by using CCSD/6-311++G** for the reactants and M06-2X/6-311+G* for the surrounding water molecules. Intermediates were characterized by all real values of the hessian matrix while transition states were characterized by one imaginary value of the hessian matrix. Open shell species were treated with unrestricted formalism. Unless otherwise noted, spin contamination values were negligibly small, $< 0.5\%$. All these calculations were performed using Gaussian 16 suite of program.³²

The rate constant of different reaction channels as well as the overall rate constant was calculated by using transition state theory³³ using equation (1)

$$k(T) = \sigma_r \Gamma(T) k_B T / h (q_{TS} / q_{R1} q_{R2}) \exp(-[?]E_0 / RT) \quad (1)$$

Values of the partition functions (q) and relative energy value ($[?]E_0$) are calculated using CCSD/6-311++G** level of theory. The value of $\Gamma(T)$, known as the tunnelling correction factors were calculated from the unsymmetrical Eckart type potential barrier method³⁴ and σ_r is the symmetry number. Other terms have usual meaning.

3. Result and discussion

3.1 Water Cluster

Fig 1 shows the TIP4P minimum energy structure of water cluster containing 50 water molecules. This cluster has been used to simulate all the reaction pathways discussed below.

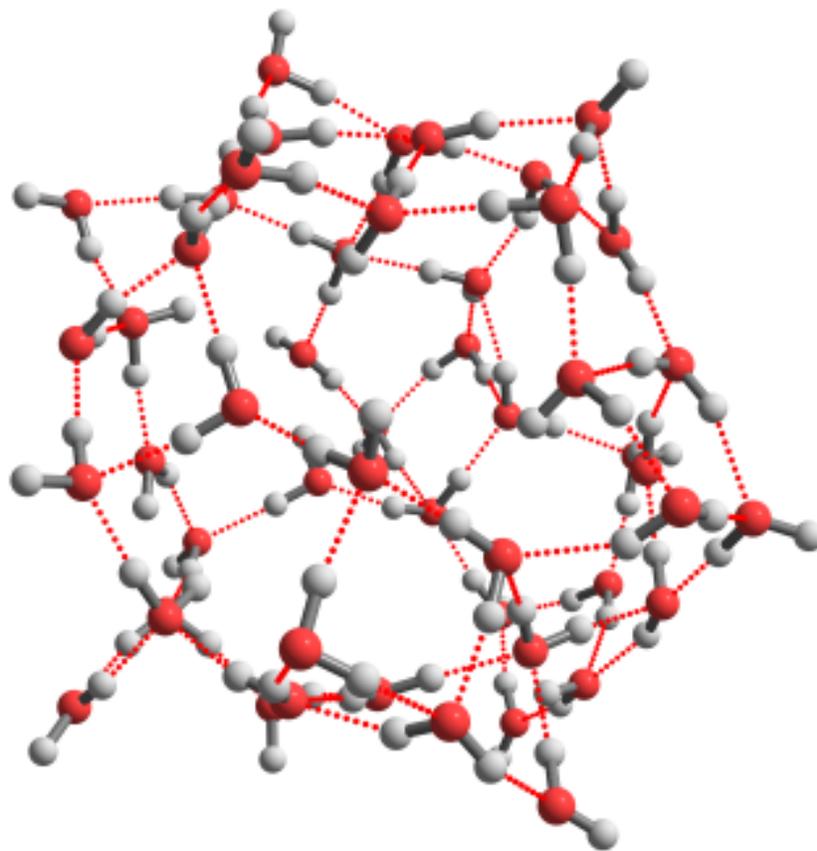


Fig 1 . TIP4P energy minimized structure of water cluster containing 50 water molecules.

3.2 Formation of Criegee Intermediate (CI): Carbonyl oxides or CIs is the source of many tropospheric reaction processes. Johnson *et.al* proved that the carbonyl oxides are produced via alkene ozonolysis having significant amount of internal energy to undergo either unimolecular or bimolecular reactions depending upon their stability.²² As tropospheric abundances of alkenes and ozone are relatively higher, it is worthwhile to study the formation of CI through the reaction between C_2H_4 with O_3 . Fig 2 shows the reaction energetic.

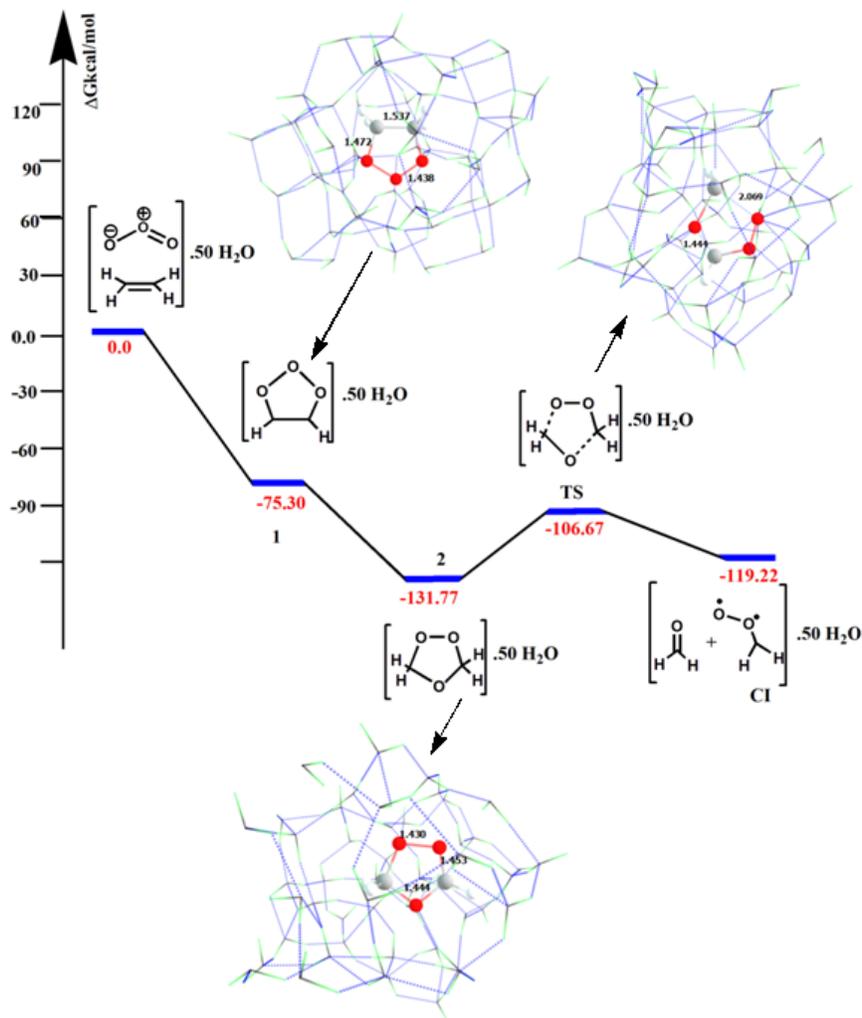


Fig 2 . Energetic for the formation of CI by the reaction of C_2H_4 with O_3 . The optimized geometries of the intermediates and transition states were also shown. Bond lengths are in Å.

CI-formation takes place via ozonolysis of C_2H_4 . First step is 1,3-dipolar cycloaddition of ozone to the double bond of ethane leading to primary ozonide or 1st molozonide, **1**. The reaction is found to be exergonic by 75.3 kcal/mol. In 2nd step, the carbonyls (as 1,3-compounds) again undergo 1,3-cycloaddition, leading to the formation of secondary ozonide **2** (more stable than primary ozonide). The 3rd step is the breaking of C-O bonds to generate the Criegee intermediate (carbonyl oxides) and H_2CO which involves a barrier of 25.1 kcal/mol. Overall, the formation of CI is exergonic suggesting the high rate of the reaction between C_2H_4 and O_3 . The studied mechanism is in tune with previously studied reactions of C_2H_4 with O_3 .^{22-28,35}

We then turned our attention to investigate all the possible reaction channels of some acids with CI. The choice of the acids namely, hydrochloric acid, formic acid and nitric acid for the reaction with CI is stimulated by their high abundance in atmosphere.

3.3 Reaction between hydrochloric acid and CI : It is generally speculated that HCl molecule inside the water cavity will become hydrated H^+ and Cl^- very quickly and therefore, will not get the time to react with CI. To investigate this, we have performed Born-Oppenheimer molecular dynamics (BOMD) simulation at M06-2X/6-31+G* for 10 ns. Figure 3 shows that the HCl molecule remains intake inside the cavity without

being hydrated till 10 ns. This interval of time may be sufficient enough for HCl to undergo reactions with CI before being hydrated. We, therefore, investigated its reaction channels with CI.

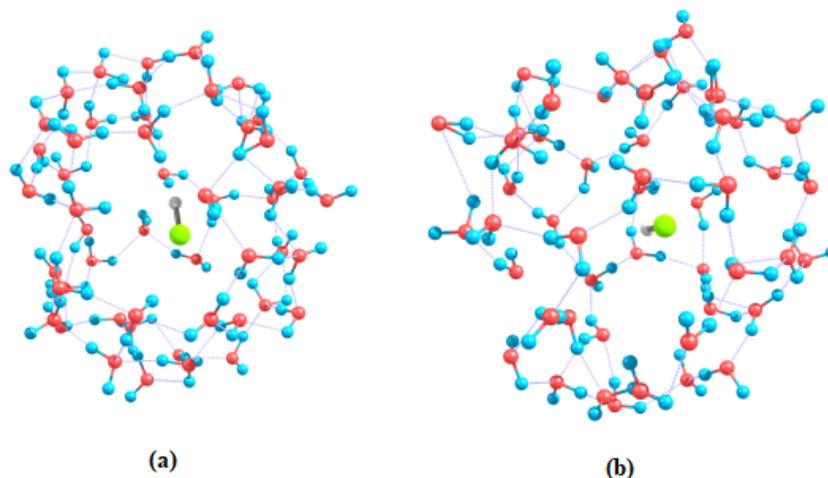


Fig 3 . Snapshots of geometry during BOMD calculations at (a) 0 ns and (b) 10 ns.

For the co-reactant HCl, two reaction channels are considered one involving the attack of H atom of HCl to the O atom of CI while the other one involves concomitant attack of H of HCl to the terminal O of CI and Cl of HCl to the C atom of CI resulting in the formation of a cyclic transition state **TS-2** (Fig 4). The energy profile diagram is shown in Fig 4.

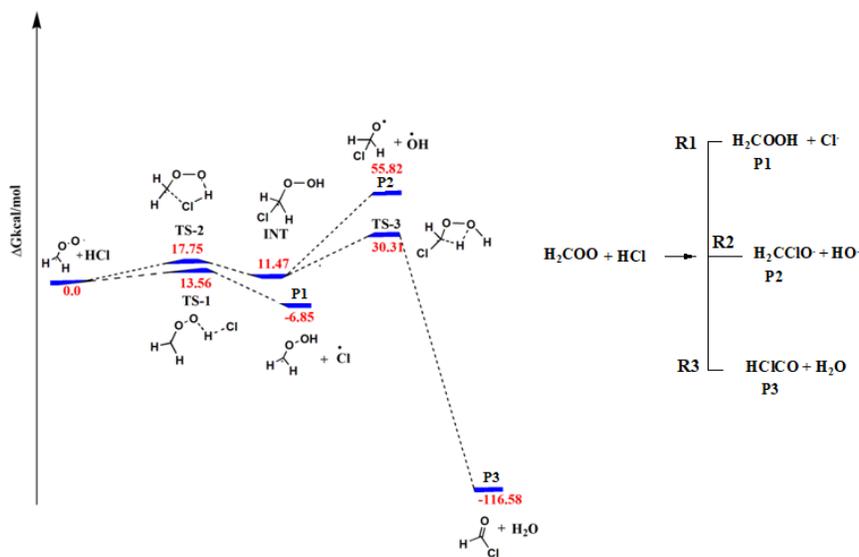


Fig 4 . Energetic of the reaction between CI and HCl in water cluster.

The first reaction route is normal proton abstraction by CI from HCl which proceed via **TS1** with a barrier of 13.56 kcal/mol and generates a chloride radical, which can further initiate chain reactions. The second reaction channel involves 1,3-insertion of HCl to CI which forms a 5-memebered **TS2** with a barrier of 17.75

kcal/mol. This **TS2** gives a relevant **INTClCH₂OOH** (chlorinated methylhydroxyperoxide) or thermally fragmented into chlorinated methoxy and hydroxyl radicals (**P2**). **INT** may lead to the most stable products chlorinated methanal and water (**P3**) via a cyclic **TS3**. The energy barrier for this process is 19.1 kcal/mol. The formation of **P3** is highly exergonic and is the most stable product.

The rate constant of each reaction channel as well as the overall rate constant of the reaction at 298 K are calculated using equation (1). It should be noted that rate constants are calculated only for the exergonic pathway. The calculated rate constants at 298 K and 1atm are $k_1 = 2.10 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ and $k_3 = 2.41 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ and the overall rate constant $k_{\text{Total}} (= k_1 + k_3)$ is $2.63 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$. The rate constant k_2 is not calculated as the reaction channel is endergonic. The calculated overall rate constant for the reaction between the CI and hydrochloric acid is in good agreement with the experimental rate constant $4.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.¹⁷

We have also calculated the percentage of the branching ratios (B.R) of each reaction channels by using the relation $\%B.R = (k_i/k_{\text{Total}}) \times 100$. The calculate value of B.R for the reaction channel R1 and R3 are 8% and 92% which indicates that the formation of **P3** via the cyclic **TS3** is the most dominant.

3.4 Reaction between formic acid and CI: Four reaction pathways have been shown for the reaction between CI and formic in this study as shown in Fig 5.

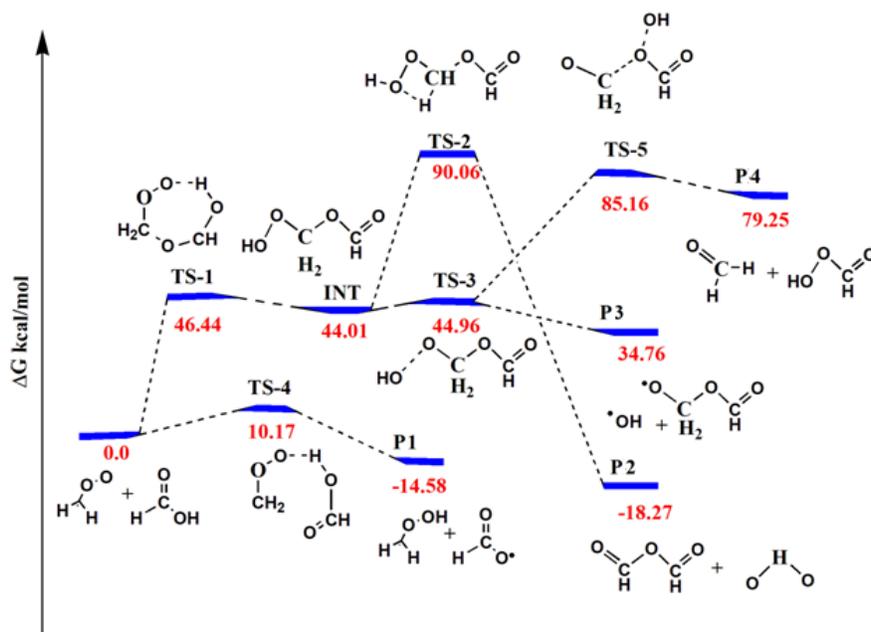


Fig 5 . Energetic of the reaction between CI and HCOOH in water cluster.

Among these pathways, three reactions are initiated through a cyclic **TS1** with a barrier of 46.44 kcal/mol which is formed due to 1,4-insertion of CI to HCOOH. The **TS1** then leads to one common intermediate hydroperoxymethylformate **INT** (HPMF). The formation of this **INT** is endergonic by 44.01 kcal/mol. This **INT** is bifurcated to **TS2** and **TS3** at the energy level of 90.06 kcal/mol and 44.96 kcal/mol respectively. The **TS2** yields highly stabilized product (**P2**) while **TS3** gives a mixture of radical product (**P3**). Another mixture of product (**P4**) is found from **TS3** via another **TS5**. The energy barrier associated with this path is very high. Another reaction route involves proton abstraction from formic acid by CI to generate an acid radical (**P1**) via **TS4** with a low barrier of 10.17 kcal/mol.

The calculate rate constant for the product **P1** formation is $2.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ while that for

product **P2** formation is $3.1 \times 10^{-13} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$. The calculate overall rate constant value k_{Total} is $2.5 \times 10^{-11} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ which is at least two times higher than the gas phase reaction ($k_{\text{Total}} = 1.1 \times 10^{-11} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$).¹⁴ The calculated B. R. suggests that the most dominating reaction channel is the formation of the acid radical (**P1**, 98%).

3.5 Reaction between nitric acid and CI: For Nitric acid, as the co-reactant for CI, three product formation pathways are shown in Fig 6.

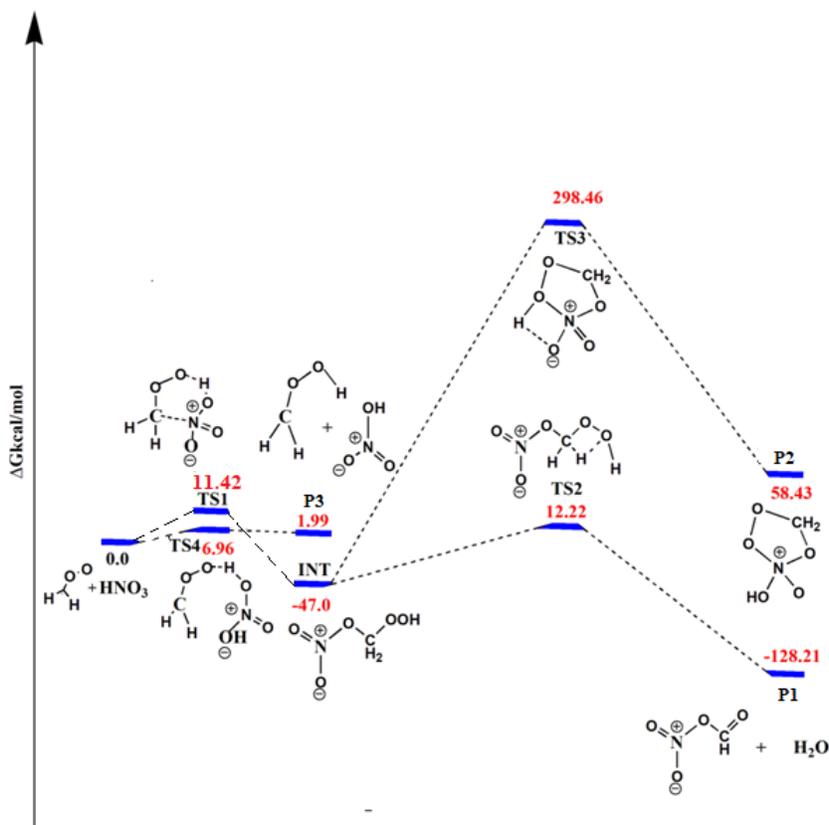


Fig 6 . Energetic of the reaction between CI and HNO₃ in water cluster.

The different sets of products can be formed for the reaction between CI and HNO₃. The formation of **P1** is exergonic while the formation of **P2** is endergonic. The attainment of these two products is sourced from same intermediate **INT** which is at the -47.0 kcal/mol in the energy profile diagram. This **INT** is attained via a transition state (**TS1**) with a barrier of 11.42 kcal/mol. The **INT** then forms two products (**P1** and **P2**) via two transition states (**TS2** and **TS3**). **TS3** lies very high in energy and thus the formation of **P2** is less likely. Third product **P3** is obtained by proton abstraction of CI from nitric acid via a transition state **TS4**. The energy barrier for the formation of **P3** is only 6.96 kcal/mol and the formation of **P3** is slightly endergonic (1.99 kcal/mol). From the energy barrier values, it is evident that proton abstraction from nitric acid will be easiest having highest rate constant values which is in agreement with previous theoretical calculations in gaseous phase.¹³

The calculate rate constant for the product **P1** formation is $3.4 \times 10^{-10} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ and the overall rate constant value k_{Total} is $6.5 \times 10^{-10} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ which slightly higher than the gas phase reaction ($k_{\text{Total}} = 5.4 \times 10^{-10} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$).¹⁷ The calculated B. R. suggests that the formation of product **P1** contributes 52% of the overall reaction channel. This suggests that other reaction channels (Fig 6) has also

significant contribution towards product distribution.

4. Conclusions

All the reaction channels of Criegee intermediate (CI) with different acids held within a water cluster having 50 water molecules have been studied using high level ONIOM method (CCSD:M06-2X). Several products have been identified with low barrier for their formation. As the atmosphere contains a large quantity of water, the reactions studied herein have a good implication towards understanding the degradation mechanism of the acids considered herein. The barrier for 1,4-insertion pathway depends on the acid. The trend of barrier for the 1,4-insertion pathway follows the order: $\text{HCOO} < \text{HCl} < \text{HNO}_3$. This is also in tune with previous experimental values of rate constants.¹⁴⁻¹⁸ This study provides all the possible pathways of degradation of these acids on reacting with CI.

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