



Theoretical study on the mechanism of chloroacetyl chloride decomposition



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ABSTRACT

The mechanism of chloroacetyl chloride (CH₂ClCOCl) decomposition has never been investigated by theoretical and experimental methods before, which is explored at the BMC-CCSD//BMK/6-311+G(d, p) level in this work. Eight pathways and ten transition states are located to search for more favorable pathways. Some dissociated pathways start from the trans-CH₂ClCOCl directly. Alternatively, the trans-CH₂ClCOCl would transform to the cis-CH₂ClCOCl. Then, the cis-CH₂ClCOCl would dissociate into the product with single or multi steps. Starting from the trans-CH₂ClCOCl, P1 (CHClCO + HCl) is the most favorable product by the rupture of C1–H1 bond and C2–Cl2 bond and the formation of H1–Cl2 bond (Pathway 1), due to the least step and the lowest barrier height. P2 (CH₂Cl₂ + CO) is the common product of both Pathway 2 and Pathway 4 those start from the trans- and cis-CH₂ClCOCl, respectively. Owing to the second lowest rate-determining barrier height, P2 is the second feasible product. P3 (CH₂Cl(O)CCL) formed by the migration of O atom from C2 atom to C1 atom is the most minor product because of the highest barrier height. Other products P4 (CH₂Cl + CO + Cl), P5 (CH₂CO + Cl₂), and P6 (CH₂ClCO(Cl)) formed by the attack of Cl2 atom to C1 atom, Cl1 atom, and O atom, respectively, are not energetically accessible because of higher barrier-consumed and/or complicated process.

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1. Introduction

Numerous research endeavors have been triggered on the halogenated hydrocarbons released into the atmosphere from various industrial processes due to their negative impact on the environment [1,2]. The released halogenated hydrocarbons would react with the atoms and radicals in the troposphere to form the secondary products, making them easier to be spread into the stratosphere. Chlorinated acetyl chloride is one of main products in the oxidation of chlorinated ethenes with relative high yields, which is also potential pollutants [3,4]. However, the research on their fate is limited so far.

The unimolecular rate constants of CHCl₂COCl and CCl₃COCl have been measured by Butler and Snelson as early as 1979 [5]. Moreover, the Arrhenius expressions were reported. However, the detailed reaction mechanism of CHCl₂COCl was not reported until 2014 [6]. Although some researchers have studied conformations, structures, and thermodynamic properties of CH₂ClCOCl [7–9], the reaction mechanism of its decomposition is still ambiguous. In this work, the unimolecular dissociation of CH₂ClCOCl is

studied using density functional theory (DFT) calculations at the BMC-CCSD//BMK/6-311+G(d, p) level with the goals to explore the reaction mechanism, obtain the products information, and determine the major products.

2. Calculation details

All the following calculations were performed using the Gaussian 09 program [10]. The geometric parameters of all involved stationary points, including reactant, products, transition states, and intermediates were optimized by the BMK method [11] with the 6-311+G(d, p) basis set [12]. Boese and Martin stated out that “To computational chemists engaged in mechanistic studies, BMK offers a single functional capable of describing all aspects of the potential surface (energetics, kinetics, structures, ...)” [11]. Further, the 6-311+G(d, p) basis set is employed since both the hydrogen atom and chlorine atom are included in the reaction. The vibrational frequencies were calculated at the same level. The transition state possesses only one imaginary frequency and the local minimum has no imaginary frequency. Starting from the transition states, the minimum-energy path (MEP) was constructed by the intrinsic reaction coordinate (IRC) [13] to confirm that two desired minima were connected. To refine the energy, the single-point

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energy corrections were performed by the composite method of BMC-CCSD (balanced multi-coefficient correlation-coupled cluster theory with single and double excitations) [14] on the basis of the optimized geometries at the BMK/6-311+G(d, p) level. In order to confirm the accuracy of BMK result, the species included in the two dominant pathways were optimized by the second-order Møller–Plesset perturbation theory (MP2) method [15,16] and Becke's three-parameter hybrid exchange functional combined with the Lee–Yang–Parr correlation (B3LYP) method [17,18] with the same basis set. To further test the accuracy of the basis set, 6-311+G(2d, 2p) basis set was applied instead of 6-311+G(d, p) basis set. Next, the energy was refined by the BMC-CCSD method on the basis of the respective optimized geometries. It is found that the barrier heights calculated at different levels are close to each other and the results are shown in Table S1 (in the supporting information). To obtain a higher performance/cost, the BMK/6-311+G(d, p) method becomes the final choice.

3. Results and discussion

3.1. Structural properties

The optimized structures of reactant, intermediates (Int1, Int2, and Int3), and products P1 (CHCICO + HCl), P2 (CH₂Cl₂ + CO), P3 (CH₂Cl(O)CCl), P4 (CH₂Cl + CO + Cl), P5 (CH₂CO + Cl₂), and P6 (CH₂-CICO(Cl)) are shown in Fig. 1 and the Cartesian coordinates and energy are shown in Tables S2 and S3 (in the supporting information). The maximum deviation between calculated and experimental results is 0.039 Å for bond length and 0.8° for angle for species CH₂Cl₂, CO, CH₂Cl, CH₂CO, Cl₂, and HCl [19–22]. The geometric parameters including bond lengths, angles, and dihedral angles of CH₂CICOCl are listed in Table 1 together with the available experimental results [23,24]. As shown in Table 1, the maximum deviation between calculated and experimental results is 0.03 Å for bond length, 3.4° for angle, and 1.6° for dihedral angle. Therefore, it is reasonable to believe that the geometries optimized at the BMK/6-311+G(d, p) level is reliable. The optimized structures of transition states are shown in Fig. 2.

3.2. Reaction Mechanism

The potential energy surface (PES) of CH₂CICOCl unimolecular decomposition at the BMC-CCSD//BMK/6-311+G(d, p) level are plotted in Fig. 3. Since the trans-conformer of CH₂CICOCl has been testified to be the most stable structure, the energy of trans-CH₂CICOCl is set as zero. There are ten transition states denoted by TS_x (x = 1–10). Eight reaction pathways denoted as Pathways 1–8 are determined and six products are found, which are listed as follows:

According to their features, they are classified into two types. One is that the trans-CH₂CICOCl dissociates into the products directly. The other is that the trans-CH₂CICOCl transforms to the cis-CH₂CICOCl firstly. Next, the cis-CH₂CICOCl decomposes to the products via single or multi steps. The relative energies of the reactant, intermediates, transition states and products for the decomposition reaction of CH₂CICOCl are listed in Table 2.

3.2.1. Pathway 1

In Pathway 1, the trans-CH₂CICOCl dissociates into CHCICO and HCl via a four-membered ring transition state TS1 that is formed by the attack of Cl₂ atom to the H1 atom. The imaginary frequency (874.1i cm⁻¹) of the transition state corresponds to the elongation of C1–H1 bond, C2–Cl₂ bond and the shortening of the H1–Cl₂ bond. Then, the product P1 (CHCICO + HCl) is released by the rupture of C1–H1 bond and C2–Cl₂ bond associated with the formation of H1–Cl₂ bond. Pathway 1 is most likely to happen with only one step and the lowest barrier height.

3.2.2. Pathway 2

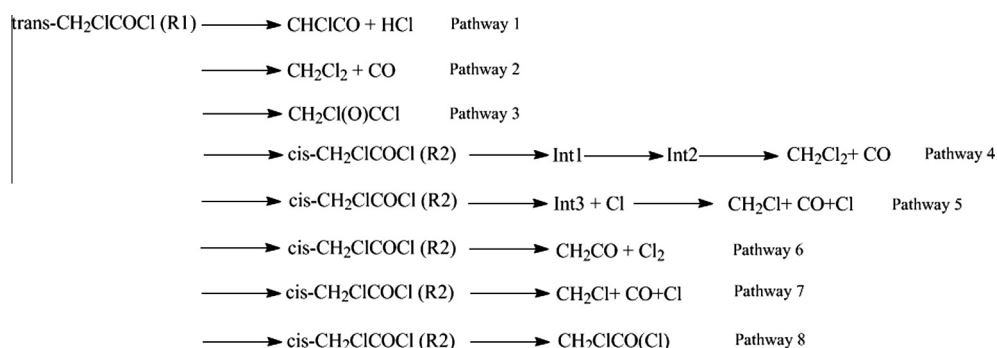
Alternatively, the trans-CH₂CICOCl undergoes both CH₂Cl₂ and CO elimination via C1–C2 bond cleavage and C1–Cl₂ bond formation to form the P2. The barrier height of Pathway 2 is 342.4 kJ/mol, which is higher than that of Pathway 1, suggesting that Pathway 2 is less favorable as compared with Pathway 1.

3.2.3. Pathway 3

Another concerted pathway is that the O atom attacks the Cl1 atom leading to the CH₂Cl(O)CCl via a four-membered ring TS3. In TS3, the O–C2 bond is elongated and the O–Cl1 bond is shortened resulting in the migration of O atom from C2 atom to Cl1 atom. However, the barrier height of TS3 is 705.8 kJ/mol, which is about 3.5 and 2 times as high as that of Pathway 1 and Pathway 2, respectively.

3.2.4. Pathways 4, 5, and 6

Besides the direct dissociation, trans-CH₂CICOCl may isomerize to cis-CH₂CICOCl. The trans- and cis-configuration are formed by the C1–C2 bond rotation. The dihedral angle O=C2–C1–Cl1 is changed from 0° to 115.2°, which agrees well with the experimental result [23,24]. Then Pathway 4, Pathway 5, and Pathway 6 start from the common complex cis-CH₂CICOCl. Subsequently, the H1 atom in Pathway 4 migrates from C1 atom to O atom to form a four-membered ring transition state TS5 with the barrier height of 288.0 kJ/mol. In the next step, the attack of Cl₂ to the C1 atom forms a triangle transition state TS6 leading to Int2. Finally, Int2 undergoes CH₂Cl₂ and CO elimination via concerted C1–C2 bond



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