Theoretical Study on the Gas Phase Reaction of Allyl Bromide with Hydroxyl Radical

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ABSTRACT

Mechanisms and reaction channels of the allyl bromide ($CH_2=CHCH_2Br$) with OH reaction are studied using quantum chemistry. It is predicted that the H(or Br)-abstraction and addition/elimination mechanisms have been revealed on potential energy surface (PES). Direct H-abstract from the —CH_2Br group of $CH_2=CHCH_2Br$ leading to h-P1 ($CH_2CHCHBr + H_2O$) is dominant. As for addition/elimination mechanism, it is shown that the reaction is initiated by the addition of OH radical to the C=C bond of $CH_2=CHCH_2Br$ to barrierlessly generate the intermediates IM1 and IM2, respectively. Multichannel RRKM theory and variational transition-state theory (VTST) are employed to evaluate the rate constants of temperature- and pressure-dependent. The calculated rate constants are in good agreement with the available experimental data. At 100 Torr with helium as bath gas, IM3 ($CH_2OHCHBrCH_2$) formed by collisional stabilization and the final products P1 ($CH_2OH + CH_2CHBr$) are the major product in the temperature range of 200–700 K and 700–1000 K, respectively. The production of $CH_2=CHCHBr$ via hydrogen abstraction becomes dominant at high temperatures (T ⩾ 1000 K). Time-dependent DFT (TD-DFT) calculations indicate that IM1-IM4, IM6, IM8 and IM9 take photolysis easily in the sunlight at the wavelength of 333 nm, 244 nm, 327 nm, 313 nm, 298 nm, 305 nm and 428 nm, once they are generated.

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1. Introduction

Halogenated organic contaminants (HOCs) mainly include the fluorinated organic compounds (FOCs), chlorinated organic compounds (COCs) and brominated organic compounds (BOCs), which show the characteristics of persistent organic pollutants in environment. Chlorinated organic compounds and brominated organic compounds contain either chlorine or bromine atoms, and thus have ozone depletion potential (ODP) [1]. Because bromine atoms and brominated organic compounds are estimated to be 40–50 times more effective than chlorine atoms and chlorinated organic compounds in ozone destruction, brominated organic compounds are particularly problematic in processes related to climate changes and play a significant role in the depletion of the stratospheric ozone [2]. Allyl bromide is widely used in industrial and agricultural production as raw materials, solvents and so on, and it can be released into environment through a variety of wastewater streams. In addition to their environmental effects, a number of studies have reported that health effects have also been identified.

For example, allyl bromide could irritate eyes, skin and respiratory system.

Experimentally, the reactions involving allyl bromide ($CH_2=CHCH_2Br$) with many radicals and molecules have been investigated extensively, including reactions such as $CH_2=CHCH_2Br$ with OH, Cl, NO_3, O_3 [3–6], respectively, which indicating that the dominant atmospheric loss pathway for allyl bromide may be reaction with OH radical. Up to date, only one experimental kinetic study have been reported the reaction of OH with $CH_2=CHCH_2Br$. In 2003, Albaladejo and Ballesteros [3] measured the rate constant of the reaction $OH + CH_2=CHCH_2Br \rightarrow$ products to be $(3.6 \pm 1.5) \times 10^{-12} \times \exp(3783 \pm 964/RT)$ cm^3 molecules^{-1} s^{-1} at P = 100 Torr and in the temperature range 228–388 K using the pulsed laser photolysis/laser-induced fluorescence technique. However, the detailed mechanisms of the degradation products of allyl bromide in atmosphere are unclear for the title reaction. Therefore, in order to detailed understand mechanistic and kinetic of the $OH + CH_2=CHCH_2Br$ reaction and understand the chemical reactivity of $CH_2=CHCH_2Br$ with OH in the atmospheric conditions, it is necessary to present the mechanistic and kinetic studies for the reaction of OH with $CH_2=CHCH_2Br$ in this work.

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2. Computational methods

Electronic structure calculations are performed with Gaussian 09 program package [7]. The optimized geometries and harmonic frequencies of all the stationary points are obtained at the M06-2X [8,9]/6-311++G(d,p) level. The nature of all stationary structure is verified by harmonic vibrational frequency calculations, namely, equilibrium species possess all real frequencies; transition states (TS) possess only one imaginary frequency. The zero-point energy (ZPE) corrections are obtained at the same level. The transition states were subjected to intrinsic reaction coordinate (IRC) [10,11] calculations to confirm connection with designated intermediates. To prove the energy prediction, the CCSD(T) [12] method with the cc-pVTZ basis set was used to calculate the single point energies based on the M06-2X/6-311++G(d,p) optimized geometries.

We choose the important product channels to calculate the rate constants using the variational transition-state theory (VTST) and multichannel Rice-Ramsperger-Kassel-Marcus (RRKM) theory [13]. In the section of the kinetic calculations, we employed the modified computer program written by Hou and Wang for the OH with allyl bromide reaction [14], and this methodology has been successfully used to deal with the complex reactions [15–19].

3. Results and discussion

The optimized structures of stationary points (the complex, intermediates, transition states, reactant and products) are listed in Figs. 1–3, along with the available experimental values, respectively. As seen in Fig. 3, the calculated bond lengths and angles at the M06-2X/6-311++G(d,p) level are in good agreement with experimental data [20], indicating that the M06-2X/6-311++G(d, p) method is suitable for predicting the geometry of the title reaction. To clarify the reaction mechanism, the potential energy surface (PES) for this reaction at CCSD(T)/cc-pVTZ//M06-2X/6-311++G(d,p) is described in Fig. 4. The ZPE, relative energies, reaction enthalpies and Gibbs free energy for all the stationary points are listed in Table 1. Table S1 displays the harmonic vibrational frequencies and the moment of inertia (au) of all species, respectively. The frequencies of CH_2CHOH, CH_2CHBr, CH_3CHO, CH_2OH, CH_2O, CH_3, H_2O, HOBr and OH are in agreement with experimental data [20]. Unless mentioned otherwise, the geometric parameters used in the discussion are the M06-2X/6-311++G(d,p) results, and the energies used are at the CCSD(T)/cc-pVTZ + ZPE level.

3.1. Reaction mechanism

As the OH radical can have either abstraction or addition/elimination mechanism, two distinguishable type initial attacks have been revealed for the radical–molecule reaction OH + CH_2=$CHCH_2$-Br, namely, the attack on H (or Br) atom and the addition to the C=C double bond (addition–isomerization–elimination). A detailed discussion on the title reaction mechanisms is given as follows.

3.1.1. Initial association
The OH-allyl bromide surface is characterized by two bound intermediates, denoted as IM1 and IM2. The initial step involves the addition of the OH radical to the C atom of the C=C bond of CH_2=$CHCH_2Br$, generating the relatively stable radicals IM1 (CH_2-OHCHCH_2Br$) and IM2 ($CH_2CHOHCH_2Br$), respectively. The reaction coordinate is complicated by an initial energy minimum at CR1, which is a weakly bound complex with a −2.38 kcal/mol barrier to further rearrangement. This typical phenomenon is also proposed by Singleton and Cvetanovic et al [21]. Therefore, the reaction of OH with allyl bromide to form IM1 and IM2 is effectively without barrier. After formed the CR1, the oxygen atom of the OH radical should rotate and add to the carbon atom of C=C double bond in CH_2=$CHCH_2Br$ via TS1 and TS2 to form IM1 and IM2, and the corresponding barrier heights are calculated to be 3.07 and 1.31 kcal/mol, respectively. The relative energy of TS1 is 1.76 kcal/-mol higher than that of TS2, Moreover, the ΔG (298 K) data for the OH addition to the central-carbon atom (TS2) is 1.22 kcal/mol lower than that addition to the terminal-carbon atom (TS1) of the C=C double bond. These results indicate that the center C-addition is slightly preferred over the terminal C-addition addition. As seen in Fig. 4 and Table 1, the formation of IM1 and IM2 are thermodynamically favorable. In the following part, we will focus on discussing the formation pathways of various products which associated with IM1 and IM2, respectively.

3.1.2. The unimolecular reaction of IM1
3.1.2.1. The CH_2OH radical formation channel.
Clearly, from IM1 (−29.32), there are two feasible pathways to form P1 (CH_2OH + CH_2CHBr). They can be written as follows

PathP1(1)R → CR1 → IM1 → IM3 → P1(CH_2OH + CH_2CHBr)

PathP1(2)R → CR1 → I M1 → IM4 → P1(CH_2OH + CH_2CHBr)
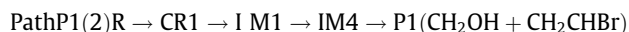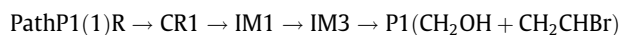
IM1 can undergo a 1,2-Br shift to form IM3 ($CH_2OHCHBrCH_2$) via transition state TS3 as shown in Path P1(1), or 1,2-H shift to form IM4 (CH_2OCH_2CHBr) via transition state TS4 as shown in Path P1(2), respectively. Finally, both IM3 and IM4 can dissociate to P1 via C—C bond rupture corresponding transition state TS5 and TS6, respectively. For IM1 → P1 conversion, two barriers must be surmounted in Path P1(1), which are 1.60 and 32.53 kcal/mol for the steps of IM1 → IM3 and IM3 → P1, respectively, it should be noted that the barrier of IM1 → IM3 is the lowest barrier among all the subsequent reaction channels of IM1 and IM2; while in Path P1 (2), the barriers are 43.64 (IM1 → IM4) and 28.13 (IM4 → P1) kcal/-mol, respectively. Due to the higher isomerization barrier, we expect that Path P1(2) should be less competitive with Path P1(1).

3.1.2.2. The CH_2O radical formation channel.
The hydrogen atom of the OH group in IM1 is migrating to the C-central atom via TS7 to form another intermediate IM5 ($CH_2OCH_2CH_2Br$). The barrier height for IM1 → IM5 is about 33.76 kcal/mol, which is 9.88 kcal/-mol lower than TS4, and 32.16 kcal/mol higher than TS3. Subsequently, IM5 decomposes to form the final products P2 (CH_2O + CH_2CH_2Br) via transition state TS8. The formation pathway of P2 can be written as

PathP2R → CR1 → IM1 → IM5 → P2(CH_2O + CH_2CH_2Br)

The barrier height for this step is 17.12 kcal/mol. However, TS8 is still lower than the reactants by 6.04 kcal/mol and TS1 by 6.73 kcal/mol, which indicating that P2 is easily yielded once IM5 is formed by increasing temperatures.

3.1.2.3. The CH_2Br radical formation channel from IM1.
Starting from IM1, only one feasible channel is associated with the formation of CH_2Br radical, which can be written as

PathP3(1)R → CR1 → IM1 → IM6 → P3(CH_2Br + CH2CHOH)
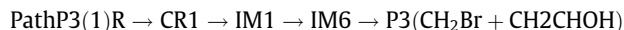
IM1 can isomerize to IM6 ($CHOHCH_2CH_2Br$) via a triangular structure transition state TS9. The barrier height of TS9 is 39.10 kcal/mol with respect to IM1, which is 5.34 kcal/mol higher than TS7 and 37.50 kcal/mol higher than TS3, as well as higher than TS1 9.09 kcal/mol. IM6, -30.36 kcal/mol relative to the initial reactants, breaks the C—C bond to give rise to P3 (CH_2Br + CH_2CHOH) via TS10 surmounting a 29.12 kcal/mol barrier height. Evidently, the rate-determining step for the formation of P3 in Path P3(1) is the H-shift step, i.e., IM1 → TS9 → IM6, because the barriers for the entrance and decomposition steps TS1 and TS10 are both lower