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The mechanism and kinetic studies for Cl-initiated oxidation of allyl acetate in troposphere

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ABSTRACT

Computational investigation on Cl-initiated oxidation of allyl acetate (AAC) including reaction mechanisms and kinetics are performed using quantum chemical method. Compared with experimental results, a more comprehensive and reasonable mechanism is proposed. For the primary reaction, seven channels (two Cl-additions and five H-abstractions) are discussed. The calculated results show that the two additional channels dominate the reaction of AAC with Cl. Further investigations of two Cl-adducts are performed in the presence of O_2 and NO. The rate constants are calculated using RRKM theory by employing the MESMER program. The total rate constant (1.39×10^{-10} cm^3 $molecule^{-1}$ s^{-1}) is well consistent with experimental data at 298 K and 760 Torr, and shows negative temperature dependence in the range of 200–500 K. Tropospheric half-life of AAC ($\tau_{1/2}$ = 4.6 h for Cl-initiated oxidation) is estimated to evaluate the atmospheric implications.

1. Introduction

Acetate esters (CH_3CO_2R, where R is an alkyl, alkenyl or Ph group) are a class of typical oxygenated volatile organic compounds (OVOCs) which have a wide range of structural diversity. Acetate esters can be emitted into the atmosphere during their use in industrial activities or by vegetation [1]. They have various industrial applications such as solvent in environmentally friendly coatings, monomer in polymerization, flavor in food and cosmetics. Acetate esters could also be detected as photolytic product of other oxygenated compounds [2,3]. The broadly uses of acetate esters especially unsaturated acetates certainly caused the emissions into the troposphere.

As one kind of alkenyl acetate, allyl acetate (AAC, shown in Fig. 1) has the vapor pressure of 31.4 mmHg at 298 K [4]. The main application of AAC is used as intermediates in production of plastics and resins [5,6]. Other applications of AAC are added into detergents and hair conditioners. It is also available as a synthetic supplement in foods and beverages [7]. In addition, AAC is also emitted through the combustion of rapeseed oil methyl ester which is used as substitution fuel [8]. AAC is highly irritant by inhalation, eye or skin contact and toxic if being swallowed [9,10]. The widespread applications of AAC in industrial inevitably lead to considerable emissions into the atmosphere as a result.

AAC is highly reactive in troposphere due to its unsaturated structure. Once being released in troposphere, AAC can be degraded by reacting with oxidants such as OH and NO_3 radicals, O_3 molecules and Cl atoms [8,11–15]. Generally, the reaction with OH radicals (with the concentration value about 2.0×10^6 molecule cm^{-3} [16]) is considered to be the most important degradation in troposphere [17,18], and it was also studied from experiment and theory [8,11,13]. However, increasing importance of the reaction for Cl atoms with VOCs in atmospheric chemistry has been gained [19–21]. Recent studies report a potential source of Cl atoms which indicated the importance of oxidation of VOCs initiated by Cl atoms may be underrated [21–23]. Atomic chlorine has the global average concentration of about 1×10^3 atoms cm^{-3} in the troposphere [24]. Nevertheless the concentration of Cl atoms would significantly increase to about 1×10^5 atoms cm^{-3} or more [25–27] in some industrial areas as well as the area near or over the ocean during the early morning [28–30]. Additionally, the reaction of VOCs with Cl atoms at rate constant is one or two order of magnitude larger than with OH radicals [31,32]. In early morning, Cl-initiated oxidation even appears to be competitive with the hydroxylation of VOCs in coastal regions.

The reaction mechanism of oxidation initiated by Cl atoms is similar to that of OH radicals [12–14,33]. Unsaturated acetates have the carbon–carbon double bond which can be attacked readily by reactive oxygen species. For example, the Cl-initiated oxidations generate Cl-adducts as primary products. Then, a series of VOCs (e.g. anhydrides, aldehydes, ketones and chlorinated organic com-

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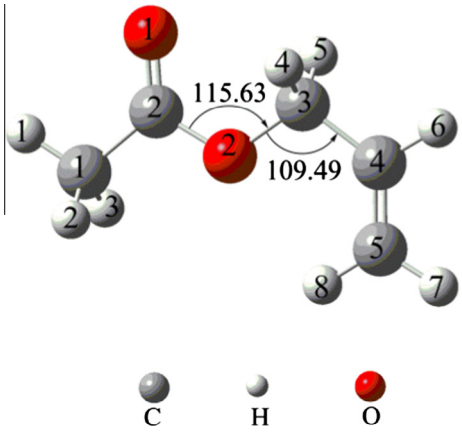

Fig. 1. The structure of AAC with labeled number. Angles are in degrees.

pounds) are formed through bimolecular reactions of Cl-adducts with O_2 and NO_x [12,14]. These oxidation processes result in secondary pollution [18]. Experimental evidence has shown that the oxidation of acetates contribute to the formation of secondary organic aerosols (SOAs) [34,35]. Additionally, these products and intermediates play an important role in modifying the atmospheric oxidation capacity and impacting on air quality, human health and climate [36,37].

Based on above background, the study on Cl-initiated reaction of AAC seems to be necessary. Up to now, two experimental studies on this reaction were published. In 2009, Blanco et al. [12] have studied the Cl-initiated oxidation of AAC at room temperature by using in situ Fourier Transform Infrared (FTIR) spectroscopy technique and relative kinetic method. The total rate constant was measured as $(1.30 \pm 0.45) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at room temperature and atmospheric pressure. In 2015, Blanco et al. again studied the products of Cl-initiated degradation of AAC in the presence and absence of NO_x using in situ FTIR [14]. They proposed the possible mechanism for AAC + Cl reaction system and gave out the main reaction products. The Cl-addition to the terminal carbon of the C=C bond was pointed as main path. However, there still exists ongoing work on this reaction. Firstly, the rate constants under a wide range of temperature and pressure are needed (only at 298 K and 760 Torr was selected in experimental study [12]). Secondly, an overall reaction mechanism is necessary for thorough understanding the chemical behaviors of AAC while it is not complete and some places are unreasonable in previous experimental study [14].

To complement the experimental study and shed light on the oxidation processes quantitatively, theoretical calculation is performed on the reaction of AAC with Cl atoms in the presence of O_2/NO. The complete reaction mechanism and favorable pathways are pointed out according to the thermodynamic data. For the kinetic calculation part, the rate constants are given out in the wide range of temperatures and pressures. To assess the atmospheric implication, the half-lives of the AAC with different oxidants have been compared in the troposphere.

2. Computational details

All of the electronic structure calculations were carried out using Gaussian 09 software package [38]. Geometry of stationary points (reactants, complexes, products, and transition states) for AAC + Cl reaction system were optimized at the M06-2X [39] level with a standard 6-31+G(d,p) basis set. M06-2X is an excellent method for its high accuracy and lower time-consumption (comparing with CBS-QB3, Table SM1 in Supplementary Material) when applying to main group thermochemistry [40] which has been used successfully in the previous studies [41–43]. The vibrational frequencies were also calculated at the same level to obtain the zero-point energy (ZPE) and confirm the nature of the stationary points (a local minimum without imaginary frequency or for transition states with only one imaginary frequency). Intrinsic reaction coordinate (IRC) [44,45] calculations were carried out at the same level to determine the connection of transition state structure between designated intermediates. In order to obtain more accurate energies, single-point energies of various species were calculated by the same method but a more flexible basis set, 6-311+G (3df,2p), based on the M06-2X/6-31+G(d,p) optimized geometries. The potential energy surfaces (PESs) were obtained at the M06-2X/6-311+G(3df,2p)//M06-2X/6-31+G(d,p) level including ZPE correction.

The rate constants for the primary reactions were calculated using Simple RRKM (for R3–R7) or the MesmerILT (for R1 and R2) method with MESMER program [46]. This program has been successfully used in the previous studies [47–50]. Calculations were based on the optimized structures, vibrational frequencies at the M06-2X/6-31+G(d,p) level of theory and energies obtained at M06-2X/6-311+G(3df,2p)//M06-2X/6-31+G(d,p) level. Helium was chosen to be the bath gas. The molecular weight of He is 4.0, and Lennard-Jones parameters are σ = 2.55 Å and ε/k = 10.2 K. The maximum grain energy is 25 kT with grains of 100 cm^{-1}. Collisional energy transfer was modeled by the single exponential-down model with ΔE_{down} of 130 cm^{-1}. For the H-abstraction reaction, the rate constants are corrected using a one-dimensional asymmetric Eckart potential.

3. Results and discussion

3.1. The initial reaction of AAC with Cl atoms

Cl-addition to C=C bond and H-abstraction from the C—H bonds are possible pathways for the initial reaction of AAC with Cl. The reaction channels of primary reaction considered in this study are presented in Fig. 2. The potential energy surface (PES) for the initial reaction is plotted in Fig. 3. The optimized geometrical structures of transition states involved in the designated reaction, with main bond lengths are shown in Fig. SM1 (in Supplementary Material). The photolysis of AAC and Cl-addition to carbonyl carbon are also considered in this paper. Comparing with the calculated results of Cl-addition to C=C bond and H-abstraction channels we can see that they are negligible. The results are shown in Supplementary Material as a reference for other similar compounds. In this paper, IM, P, and TS are the abbreviations for intermediate, product, and transition state respectively.

Two carbon atoms on the double bond in AAC are different. Thus, two Cl-addition pathways (R1, Cl-addition to C5 and R2, Cl-addition to C4) should be considered. The results of flexible potential energy surface scanning show that the two Cl-addition processes could occur barrierlessly in atmosphere (given in Fig. SM2). Two radical adducts (IM1, $CH_3C(O)OCH_2CHCH_2Cl$ and IM2, $CH_3C(O)OCH_2CHClCH_2$) are formed with exothermic energy of 22.6 and 21.3 kcal mol^{-1}, respectively. The bond lengths of Cl—C5 (1.848 Å) in IM1 and Cl—C4 in IM2 (1.851 Å) are similar.

Five H-abstraction processes (shown in Fig. 2, R3–R7) are considered because there are five kinds of different H atoms (H1, H4, H6–H8) existed in AAC. R3 and R4 have pre-reactive complexes, IM03 and IM04. Through transition states TS1 and TS2, IM3 and IM4 are formed, respectively. These two H-abstraction processes are exothermic with energy barriers of 6.2 and 2.0 kcal mol^{-1}. For R5–R7, formations of post-reactive complexes (IM05, IM06 and IM07) are followed by the productions of IM5, IM6 and IM7 via