



Mechanistic and kinetic investigations on the ozonolysis of isopropenyl acetate and propenyl acetate in atmosphere



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ABSTRACT

The ozonolysis of isopropenyl acetate (IPA) and propenyl acetate (PA) are investigated by quantum chemical method. The detailed reaction mechanisms are provided, including the formation and decomposition of the primary ozonide (POZ), the formation of the secondary ozonide (SOZ) and further reactions of Criegee intermediates. By means of the CBS-QB3 composite method, the potential energy surfaces (PESs) are obtained and the major products are identified, respectively. Based on the PESs calculations, master equation (ME) calculations are used to examine the rate constants. Finally, the lifetimes of IPA and PA in troposphere are estimated.

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1. Introduction

Acetates are important volatile organic compounds (VOCs) which were released into the atmosphere from both anthropogenic and natural sources. These compounds have extensive industrial applications, for example, being used as solvents, surfactant and polymer monomer. Because of their high volatility, large quantities of acetates could escape into the atmosphere every year. They could also be released by the tropospheric degradation of oxygenated compounds (especially ethers) [1,2]. Besides, acetates have been detected as important organics of vegetational emissions [3]. Once acetates are released into the atmosphere, their degradation are expected to be initiated by oxidants in the air and contributed to the formation of photooxidant [4,5].

Nowadays, more and more attentions have been paid on the ozonolysis of acetates due to their effects on indoor and outdoor environment. Mechanism of the ozonolysis of acetates may be similar to that of the reaction of ozone with alkenes: $O_3 + R_1R_2C = C(R_3)OC(O)CH_3 \rightarrow \alpha (R_1C(O)R_2 + CH_3C(O)OC(R_3)OO) + (1 - \alpha) (R_3C(O)OC(O)OCH_3 + CH_3C(O)OC(R_3)OO)$ [6,7]. The main products of the ozonolysis of acetates are ketones or aldehydes ($R_1C(O)R_2$), and both of them have a significant effect on environment. For example, formaldehyde is a kind of definitely primary indoor air pollutant. Ketones and aldehydes could be oxygenated to form carboxylic acids, which could stabilize atmospheric pre-nucleation

clusters [8]. $CH_3C(O)OC(R_3)OO$ and $CH_3C(O)OC(R_3)OO$ are energy-rich Criegee intermediates which subsequently undergo a series of reactions with various atmospheric compounds (OH, RO_2 radicals, SO_2 , NO_x , O_2 , and H_2O) [9]. Additionally, the stabilized Criegee intermediates are the source of OH radicals, H_2O_2 , organic acids, and aldehydes, through bimolecular reactions with atmospheric oxidants (particularly NO, H_2O) [6]. These products make great impact on the atmospheric oxidation capacity and do harm to the life on Earth [10–12]. Also they play a certain role in the formation of secondary pollutant and SOAs [13–15]. Therefore, it is necessary to investigate the mechanism of ozonolysis of acetates in order to understand the complex environmental decomposition process. Kinetic data is indispensable to obtain the lifetime of acetates emitted into the atmosphere and properly comprehend its environmental implications.

The acetate ozonolysis has been studied from several theoretical and experimental investigations. Roger Atkinson et al. studied the gas-phase reaction of O_3 with cis-3-Hexenyl acetate experimentally in 1995 [16]. They reported the rate constants and pointed out the yield of OH radicals (0.16). The kinetic and mechanistic experimental studies for the ozonolysis of trans-2-hexenyl acetate and cis-3-hexenyl acetate were performed by Eric Grosjean et al. in 1996 and 1997, respectively [17]. The primary products and the rate constants were identified. Sle Calve et al. studied kinetic of O_3 reactions with allyl acetate and isopropenyl acetate (IPA) using the pulsed laser photolysis-laser induced fluorescence technique [18]. The relative rate constant was given as $(0.7 \pm 0.2) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at $(298 \pm 4) \text{ K}$ and 1 atm.

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Obviously, the rate coefficient for the reaction of O₃ with isopropenyl acetate has been studied over a narrow range of temperatures, which cannot satisfy environmental temperature change. Picquet-Varrault et al. reported the kinetic and mechanistic experimental study for the reaction of vinyl acetate with O₃ in dry condition [19]. He et al. studied the ozonolysis of allyl acetate and vinyl acetate by quantum chemistry method, in which the rate constants and the primary products were proposed [20,21].

It is necessary to study the rate coefficients over the range of temperatures typically prevailing in the troposphere, which are not sufficient in previous researches [18]. Except for kinetic data, the feasible mechanism and detailed products of the reaction which would allow an assessment of potential environmental impacts have been little provided. In addition, the mechanism and kinetics for the ozonolysis reaction of propenyl acetate (PA) in gas-phase are still unavailable. Hence, the ozonolysis of IPA and PA merit a theoretical study to analyze the reaction mechanism and to estimate rate constants over the wide range of temperatures.

This study aims to perform a systematic theoretical research for the gas-phase mechanism of the reactions of ozone with IPA and PA by high-level Density Functional Theory (DFT) calculations. The formation of the primary ozonides (POZs) from IPA + O₃ and PA + O₃, the subsequent decomposition of POZs, the formation of the secondary ozonides (SOZs) and the further reactions of Criegee intermediates in the presence of H₂O or NO are considered in this study. Additionally, the rate constants were estimated using the energy-grained master equation (ME) to obtain the branching ratios of reaction pathways and the atmospheric lifetimes of IPA and PA.

2. Computational details

In this paper, all calculations are performed using GAUSSIAN03 suite of program package [22]. The B3LYP level with 6-31G(d,p) basis set are employed to optimize structures of stationary points and transition states. The CBS-QB3 composite method [23–25] is used in further calculations in order to obtain the accurate energetic parameters. CBS-QB3 method can provide accurate characteristics of reaction (energy barrier, activation enthalpy, free energy of activation, formation enthalpy, changes in free energy, etc) [26–28]. To confirm the reliability of the computational method, these parameters were also calculated using an combined methods of B3LYP [29] and CCSD(T) [30] (CCSD(T)/6-31G(d)+CF//B3LYP/6-31G(d,p) method) which is proposed by Zhang et al. [31,32]. Intrinsic reaction coordinates (IRC) [33,34] calculations of each transition state are performed to ascertain the transition state actually connect the expected reactants with intermediates or products for each elementary reaction.

The energy-grained master equation (ME) has been described at full length in previous researches [35–37], and are undertaken to study the rate constants on the basis of the PES results (the result of the CBS-QB3 method). ME is effective method to calculate the rate constants for modeling reactions with several connected energy wells and many product channels. All ME calculations are carried out using the open source program MESMER [38]. The master equation is

$$\frac{d\mathbf{p}}{dt} = M\mathbf{p} \quad (1)$$

where \mathbf{p} is the population distribution vector and M is the collision/reaction matrix that describes the collisional energy transfer between the states and reaction from the energized states. The exponential down model has been employed for calculating collisional energy transition probabilities.

The microcanonical rate coefficient $k(E)$ for each elementary reaction in this paper follows the below equation:

$$k(E) = \frac{W(E)}{h\rho(E)} \quad (2)$$

Here, $W(E)$ is the sum of rovibrational states at the optimized transition state geometry, and ρ is the density of rovibrational states of the isomer.

The branching ratio (R) for the different pathways was determined on the basis of rate constants:

$$R_i = \frac{k_i}{\sum_i k_i} \quad (3)$$

where k_i is the forward reaction rate constant for the i th channel.

3. Results and discussion

Before further discussion of the reaction mechanism, it is worthy to remark on the accuracy of the methods (CBS-QB3 and CCSD(T)/6-31G(d)+CF//B3LYP/6-31G(d,p) which will be labeled as CCSD(T) in the following) used in this work. Due to lacking of experimental data for the title reactions, the reaction of congener compound, vinyl acetate, with H₂ (CH₃C(O)OCH=CH₂ + H₂ → CH₃C(O)OCH₂CH₃) are applied to examine the reliability of these two methods. In our results, the above reaction is exothermic by 29.76 kcal/mol for CBS-QB3 and 28.66 kcal/mol for CCSD(T), respectively. Comparing with the experimental value of (31.10 ± 0.072) kcal/mol [39], the CBS-QB3 value is more reliable than that of CCSD(T)'s. Hence, CBS-QB3 energies are employed in the following discussion except specified. Besides, calculated the CCSD(T) energies are shown in Table SM-2 as supplementary data.

The detailed reaction mechanism of IPA + O₃ reaction is depicted in Fig. 1 while that of PA are shown in Fig. SM-1 (supplementary material). Fig. SM-2 shows the geometry structures of all the transition states involved in the reactions of O₃ with IPA and PA as well as the bond lengths of relative active sites. The potential energy profiles corresponding to the title reactions are shown in Fig. 2.

3.1. The formation and decomposition of the primary ozonides

3.1.1. IPA and O₃

The ozonolysis of IPA begins with cycloaddition of O₃ molecule to the C=C bonds of IPA according to our previous work [20,21]. This process is initialized with the formation of a van der Waals complex, IM1, of whom the distance between C1–O3 and C2–O5 are 2.859 Å and 3.009 Å, respectively. IM1 lies 1.67 kcal/mol below IPA + O₃, as seen in Fig. 2. Then the primary ozonide (IM2) is produced via a transition state TS1. IM2 is a five-membered ring (C1–O3–O4–O5–C2) intermediate of which the bond lengths of C1–O3 and C2–O5 are 1.427 Å and 1.406 Å, respectively. IRC calculations confirmed that TS1 can connect the initial reactants (IPA and O₃) with the IM1. This process is high exothermic by 61.30 kcal/mol with a moderate energy barrier of 2.15 kcal/mol. As a five-member-ring intermediate, IM2 is inclined to stabilize via two different self decomposition processes, as shown in Fig. 1. First, IM2 may decompose through the cleavage of C1–C2 and O4–O5 bonds, followed by the formation of acetic anhydride (P1) and CH₂OO (IM3) with exothermic value of 2.61 kcal/mol. TS2 is corresponding transition state which lies 15.57 kcal/mol above IM2. The other path proceeds with the cleavage of the C1–C2 and O3–O4 bonds leading to the formation of P2 (HCHO, formaldehyde) and biradical intermediate IM3 (CH₃C(O)C(CH₃)O₂). The energy barrier and reaction heat of this channel are 21.74 and 5.43 kcal/mol, respectively. Taking the energy barriers and reaction

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