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Mechanistic and kinetic study of the gas-phase reaction of vinyl acetate with ozone

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The reaction mechanisms of vinyl acetate with O_3 are investigated by performing Density Functional Theory (DFT) calculations as an attempt to investigate the photooxidation reaction of acetate in the atmosphere. The detailed reaction mechanisms are proposed. The potential energy surface profiles (PESs) are constructed. Several products (formaldehyde, heroperoxymethyl formate and formic acetic anhydride) resulting from the gas phase reactions are identified by comparing with the experimental results. The experimentally uncertain dominant product of CH_2OO is confirmed to be heroperoxymethyl formate. The experimentally unknown mechanism for the formation of formic acetic anhydride from CH_3OCHOO is proposed. Rate constants of the reaction over the temperature range of 200–2000 K are obtained by using Rice–Ramsperger–Kassel–Marcus (RRKM) theory based on the above PES calculations. The rate constants are independent on pressure.

1. Introduction

Vinyl acetate (VAC, $CH_2{=}CHOC(O)CH_3$) is a synthetic organic ester and has been widely employed in different industries. The major use of VAC is that it is selected as intermediates for the synthesis of a range of polyvinyl acetate and vinyl acetate co-polymers. These polymer products are used in water-based paints, adhesives, foils, and paper coatings, etc. (HSDB, 1994). VAC is also used in safety glass interlayers and in hair sprays (Graedel et al., 1986). US EPA found that the annual production and/or importation volumes are more than 1 million pounds (U.S.EPA, 2006), and thus it is listed in the OECD (Organization for Economic Co-operation and Development) integrated high-production volume (HPV) database.

The release of VAC into the environment is likely to occur and will exist mainly as vapors because its vapor pressure is high (89 mmHg at 298 K). VAC is also emitted by carpets containing PVC (Hodgson et al., 1993). The annual emissions from facilities were estimated to be 3855 pounds of vinyl acetate in California (CARB, 2000). VAC is federal hazardous air pollution and identified as a toxic air contaminant in April 1993 under AB2728.

Upon its release into the troposphere, VAC will undergo either photolysis or photochemical transformation by OH radicals and ozone during daytime and by nitrate radicals (NO_3) and ozone during the nighttime. These chemical reactions may play an increasingly important role in the chemistry of the polluted troposphere such as the contribution to the formation of ozone and secondary pollutants (Mellouki and Thiault, 2006). Reaction mechanism and kinetic information on the troposphere oxidation of VAC is essentially important to assess the possible effect of VAC to air pollution in indoor and outdoor. In general, the reaction of OH radicals with VAC is the dominant atmospheric loss process among these various reactions (Picquet-Varrault et al., 2010). However, ozonolysis of VAC may also play an important role in the formation of SOA. Picquet-Varrault et al. (2010) have performed the kinetic and mechanistic experimental study for the reaction of VAC with O_3 in dry conditions. In this study, the rate constant is given as $(3.0 \pm 0.4) \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}, and the primary products have been identified as formic acetic anhydride and formaldehyde. The possible ozonolysis reaction mechanism has been proposed according to their experimental observation. However, several questions can not been solved in this paper: a) no mechanism can be proposed to explain the formation of formic acetic anhydride from the biradical ($CH_3C(O)OCHO_2$) under dry conditions; b) the products of the radical CH_2O_2 can not be detected and remains unidentified; c) the yield of formic acetic anhydride is close to unity while that of the formaldehyde is detected to be 0.20 ± 0.06 in which the carbon is imbalance obviously. Based on above several points, theoretical investigations on the detailed products and the estimated rate constants covering the whole temperature range of practical interest are performed.

The accurate Potential Energy Surfaces (PESs) which can provide the geometrical structures of all stationary points involved in the

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reactions can be constructed by the theoretical calculations. PESs can not only assist to judge whether a product channel is favorable or not, but also can provide new findings that could not be observed experimentally (Yu et al., 2011; Zhang et al., 2008a,b, 2009a,b, 2010). Thus, as an experimental verification and supplement we investigate the O_3-initiated atmospheric photooxidation reaction of VAC in troposphere using theoretical method. In this work, not only the reaction paths previously proposed by experimental study are reconsidered but also the new possible reaction paths which can help explain the previous experimental observations are given.

2. Computational details

2.1. Electronic structure calculations

All calculations reported in this article are performed with GAUSSIAN03 suite of program package (Frisch et al., 2003). Vinyl acetate (VAC, $CH_2{=}CHOC(O)CH_3$) and O_3 are selected as the reactants. The geometrical parameters of reactants, intermediates, transition states and products on the PESs of the system are fully optimized at the B3LYP/6-31 + G(d,p) level of theory which is sufficient to calculate the frequencies and geometrical parameters of all stationary points (Zhang and Zhang, 2005, 2002; Zhang et al., 2002). The corresponding harmonic vibrational frequency calculations at the same level are used to characterize all stationary points as either minima (no imaginary frequencies) or transition states (one imaginary frequency), obtain zero-point energies (ZPEs) and calculate the rate constants. To verify that transition states actually connect to the expected reactants, intermediates and products for each reaction, intrinsic reaction coordinate (IRC) (Gonzalez and Schlegel, 1989, 1990) calculations are performed. To accurately obtain the energetic parameters, further calculations with the CBS-QB3 method (Montgomery et al., 1999) are made on the basis of B3LYP/6-31 + G(d,p)-optimized geometries. The energies emerging in this paper include the ZPE corrections unless otherwise specified. The secondary reactions are investigated in the presence of H_2O and NO in order to understand the possible reaction mechanisms of secondary pollutants formation from the O_3-initiated atmospheric reaction of VAC.

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2.2. Rate constant calculations

For the major product channels, rate constants have been computed using Rice–Ramsperger–Kassel–Marcus (RRKM) theory and master equation calculations on the basis of above PESs calculations. This method has been successfully used in the previous study (Hou and Wang, 2007). The microcannonical rate constants are calculated using the following equation:

$$k_i(E) = \alpha_i \kappa_i \sqrt{\frac{I_i^{\neq}}{I_j^{\mathrm{IM}}}} \, \frac{N(E - E_i^{\neq})}{h\rho_j(E)} \quad i = 1,2,3; \; j = 1. \tag{1}$$

Here α_i is the statistical factor for the path degeneracy; κ_i is tunneling factor which is considered using the one-dimension asymmetrical Eckart potential (Johnston and Heicklen, 1962); The Eckart potential was determined by three parameters, that is, barrier height, reaction heat, and imaginary frequency. $I_i^{\neq}, I_j^{\mathrm{IM}}$ are the moments of inertia ($I_a I_b I_c$) of transition state and intermediate j; $N(E - E_i^{\neq})$ is number of states and the energy above the barrier height $E_i^{\neq}$ for i; h is Planck's constant; $\rho_j(E)$ is the density of states at energy E of the intermediate j; Beyer–Swinehart algorithm (Astholz et al., 1979; Stein and Rabinovitch, 1973) is employed to calculate the density of states and number of states.

Equation for calculating collision deactivation rate is as follows:

$$\omega = \beta_c Z_{\mathrm{LJ}}[\mathrm{CO}] \tag{2}$$

Here, β_c is the collision efficiency calculated by Troe's weak collision approximation (Troe, 1977) with energy transfer parameter $-\langle \Delta E \rangle$. $-\langle \Delta E \rangle$ is estimated by the Lim and Gilbert's biased random walk (BRW) model ($T = 200{-}2000$ K): $-\langle \Delta E \rangle/\mathrm{cm}^{-1} = 0.52T + 6$ for CO. Z_{LJ} is the Lennard–Jones collision frequency. [CO] is the concentration of carbon monoxide which is selected as an OH scavenger. The above parameters at 290 K and 760 Torr have been calculated to be: $-\langle \Delta E \rangle = 156.8$, $\beta_c = 0.331$, and $Z_{\mathrm{LJ}} = 1.88 \times 10^{-10}$.

3. Results and discussion

3.1. The reaction mechanism of VAC with O_3 radicals

O_3 addition to the C=C bond must be a possible pathway since there is one carbon–carbon double bond in VAC. Only one possible reaction pattern is considered for the reaction of VAC with O_3: O_3-addition to C1=C2 double bonds.

The mechanism based on the calculated results is shown in Fig. 1. Fig. 2 gives the optimized geometries of transition states involved in the reaction of O_3 with VAC. The potential energy surfaces corresponding to the ozonolysis of VAC reaction is shown in Fig. 3(a, b and c). The main bond lengths of all stationary points are labeled in Table S1.

In the ozonolysis reaction of VAC, the first step proceeds by the addition of O_3 to the two carbons and forms a van der Waals complex, IM1. And then an ozonide (IM2) is formed:

$$\mathrm{R} + \mathrm{O_3} \rightarrow \mathrm{IM1} \quad \Delta H = -1.10 \ \mathrm{kcal\ mol^{-1}} \tag{R1}$$

$$\begin{aligned} &\mathrm{IM1} \rightarrow \mathrm{TS1} \rightarrow \mathrm{IM2} \quad \Delta E = 0.08 \ \mathrm{kcal\,mol^{-1}} \\ &\quad \Delta H = -57.10 \ \mathrm{kcal\,mol^{-1}} \end{aligned} \tag{R2}$$

IM1 is a pre-complex in which the distances between O and C are 2.630 (C1–O3) and 2.765 Å (C2–O5), respectively. The energy of IM1 is 1.10 kcal mol^{-1} lower than the total energy of the separate reactants (VAC and O_3). And then the adduct, $CH_2O3CHOC(O)CH_3$ (O_3-VAC, IM2) is formed through the transition state TS1 which has the barrier height of 0.08 kcal mol^{-1}. In TS1, the additions O3 and O5 atoms are concerted and the bond lengths of C1–O3 and C2–O5 are 2.229 and 2.369 Å which are 0.401 and 0.396 Å shorter than those of the IM1, respectively. These long C–O bonds indicate that the TS1 is reactant-like transition state structures. IRC calculation shows that TS1 does connect IM1 and IM2. IM2 is a five-membered ring (C1–O3–O4–O5–C2) in which the bond length of C1–O3 is 1.423 Å which is shortened by 45.9% and 36.2% with respect to the corresponding one in IM1 and TS1, respectively, and the bond length of C2–O5 is 1.406 Å which is shortened by 49.2% and 40.7%, respectively. The energy of IM2 is 56.00 kcal mol^{-1} lower than that of IM1. This low barrier energy and high exothermic energy of this process mean that this O_3 addition reaction can occur readily.