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Mechanism and kinetic studies for OH radical-initiated atmospheric oxidation of methyl propionate

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HIGHLIGHTS

- ► Mechanism and kinetics for OH-initiated reaction of methyl propionate were studied.
- ► Detailed reaction mechanism was proposed.
- ► The overall rate constant have been obtained.
- ► The atmospheric lifetime determined by OH radicals is about 15.5 days.

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ABSTRACT

DFT molecular orbital theory calculations were carried out to investigate OH radical-initiated atmospheric oxidation of methyl propionate. Geometry optimizations of the reactants as well as the intermediates, transition states and products were performed at the B3LYP/6-31G(d,p) level. As the electron correlation and basis set effect, the single-point energies were computed by using various levels of theory, including second-order Møller–Plesset perturbation theory (MP2) and the coupled-cluster theory with single and double excitations including perturbative corrections for the triple excitations (CCSD(T)). The detailed oxidation mechanism is presented and discussed. The results indicate that the formation of 3-oxo-methyl propionate ($HC(O)CH_2C(O)OCH_3$) is thermodynamically feasible and the isomerization of alkoxy radical IM17 ($CH_3CH(O)C(O)OCH_3$) can occur readily under the general atmospheric conditions. Canonical variational transition-state (CVT) theory with small curvature tunneling (SCT) contribution was used to predict the rate constants. The overall rate constants were determined, $k(T)(CH_3CH_2COOCH_3 + OH) = (1.35 \times 10^{-12})\exp(-174.19/T)$ cm^3 $molecule^{-1}$ s^{-1}, over the possible atmospheric temperature range of 180–370 K.

1. Introduction

Methyl propionate ($CH_3CH_2COOCH_3$) is used as industrial solvent and synthesis reagent during the manufacture of cellulose derivative, fragrances and flavoring agents (Budavari and O'Neil, 1996; Lewis, 1993; Cavalli et al., 2000). Just in China, 30 thousand tons of methyl propionate was produced in 2010 (China survey, 2011). It can also be detected as a volatile component from some fruits (Snyder, 1992; Bartley and Schwede, 1989; Dirinck et al., 1984) and identified from various waste exudates (Wilkins and Larsen, 1996). Methyl propionate can be released to the atmosphere and exists mainly in the gas phase because of the high vapor pressure (84 mmHg at 298 K) (Bidleman, 1988; Daubert and Danner, 1989). The increasing use of methyl propionate as the replacement for traditional solvents leads to increasing concentration in the atmosphere where it can undergo transport and chemical transformation (Cavalli et al., 2000). To assess the atmospheric behavior of pollutants, it is critical to know their atmospheric reactions.

The atmospheric removal or transformation of gaseous methyl propionate involves wet and dry deposition, photolysis, and oxidation reactions with OH, NO_3 and O_3. Reaction with Cl atoms may also be important in certain locations during certain times of the year (Finlayson-Pitts, 1993; McGillen et al., 2006; Eladio et al., 2003). The wet and dry deposition of gaseous methyl propionate is of relatively minor importance as a removal pathway because of its low Henry's law coefficients (6.1 M atm^{-1}) (Hine and Mookerjee, 1975). Photolysis of esters appears to be insignificant in the lower atmosphere (Calvert and Pitts, 1966). As a sort of saturated ester,

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methyl propionate is therefore expected to react with ozone hardly. As discussed in the former references (Atkinson, 1991; McGillen et al., 2006; Smith and Plane, 1995), except for typical species include olefins that are C_4 and higher, terpenes, many aromatics, and sulfur-containing alkanes, NO_3 radicals initiated abstraction is a negligible tropospheric loss process compared to OH radicals. Among the various oxidants, OH radicals play the most essential role in determining the oxidation power of the atmosphere. The reaction of methyl propionate with OH radicals is considered to be a dominant removal process. The atmospheric oxidation of methyl propionate may significantly contribute to the formation of second contamination belong to the components of the photochemical smog in urban areas.

Current available database concerning the atmospheric chemistry of methyl propionate is limited. Calve performed the experimental study on OH-initiated reactions of a series of methyl esters using the pulsed laser photolysis-laser induced fluorescence (PLP-RF) technique over the temperature range of 253–372 K (Calve et al., 1997). Arrhenius expression for the reaction of methyl propionate with OH was derived as follows: $k = (1.45 \pm 0.42) \times 10^{-12}$ exp − $(148 \pm 86)/T$ cm^3 $molecule^{-1}$ s^{-1}, and the rate constant was given as $(0.83 \pm 0.09) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K. Absolute rate coefficients were measured for the reactions of a series of esters with Cl at the room temperature and over the pressure range of 15–60 Torr, using the PLP-RF technique (Alberto et al., 1998). The rate constant for methyl propionate with Cl was determined as $(1.98 \pm 0.26) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}. Cavalla studied the atmospheric oxidation of methyl propionate by OH and Cl radicals in the presence of NO_x in 740 Torr of air at 296 ± 2 K using smog chamber FTIR techniques (Cavalli et al., 2000). Relative rate techniques were used to measure the rate constants, $k(OH + CH_3CH_2C(O)OCH_3) = (9.29 \pm 1.13) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}, $k(Cl + CH_3CH_2C(O)OCH_3) = (1.51 \pm 0.22) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}. Andersen investigated the products for the reaction of methyl propionate with OH radicals (Andersen et al., 2011).

However, there is a notable shortage of direct experimental data associated with the reaction mechanism, largely due to lack of efficient detection schemes for radical intermediate species. Quantum calculation is especially suitable for establishing whether a reaction pathway is feasible or not. In this paper, we have carried out a theoretical study of the application of quantum calculations for the OH-initiated atmospheric oxidation of methyl propionate in order to find out favorable reaction pathways and sites. Elucidation of the reaction mechanism is very challenging due to the inherent complexity. The potential energy surface is useful to explain the experimentally observed degradation products, thermochemical properties, and rate coefficients.

2. Computational method

The electronic structure calculations were performed with the Gaussian 03 software package (Frisch et al., 2003). Geometries of the reactants, intermediates, transition states, and products were optimized with the aid of Becke's three-parameter hybrid method employing the LYP correction function (B3LYP) in conjunction with the split valence polarized basis set 6-31G(d,p). The harmonic vibrational frequencies were also calculated at the same level to determine the nature of the stationary points, the zero-point energy (ZPE), and the thermal contribution to the free energy of activation. The intrinsic reaction coordinate (IRC) analysis was carried out to confirm that each transition state connects to the right minima along the reaction path (Fukui, 1981). The DFT geometries were then used in the single-point energy calculation at the frozen-core second-order Møller–Plesset perturbation theory (MP2) and the coupled-cluster theory with single and double excitations including perturbative corrections for the triple excitations (CCSD(T)) with various basis sets. The single-point energies were further corrected. The procedure involved determination of a correction factor associated with the basis set effect at the MP2 level and subsequent correction to the energy calculated at a higher level of electron correlation with a moderate size basis set. A correction factor, CF, was determined from the energy difference between the MP2/6-31G(d) and MP2/6-311++G(d,p) levels. The values of calculated energies at the CCSD(T)/6-31G(d) level were then corrected by the MP2 level correction factors, corresponding to the CCSD(T)/6-31G(d)+CF level of theory (Lei and Zhang, 2001; McGivern et al., 2000).

Rate constants were estimated by using the canonical variational transition-state (CVT) theory (Baldridge et al., 1989; Gonzalez-Lafont et al., 1991; Garrett and Truhlar, 1979) with the small curvature tunneling (SCT) (Fernandez-Ramos et al., 2007) method. The CVT rate constant for temperature T is given by:

$$k^{\mathrm{CVT}}(T) = \min_{S} k^{\mathrm{GT}}(T,s) \tag{1}$$

where

$$k^{\mathrm{GT}}(T,s) = \frac{\sigma k_B T}{h}\frac{Q^{\mathrm{GT}}(T,s)}{\Phi^{R}(T)}e^{-V_{\mathrm{MEP}}(s)/k_{\mathrm{B}}T} \tag{2}$$

where $k^{\mathrm{GT}}(T, s)$ is the generalized transition state theory rate constant at the dividing surface s, σ is the symmetry factor accounting for the possibility of more than one symmetry-related reaction path, k_B is Boltzmann's constant, h is Planck's constant, $\Phi^R(T)$ is the reactant partition function per unit volume, excluding symmetry numbers for rotation, and $Q^{\mathrm{GT}}(T, s)$ is the partition function of a generalized transition state at s with a local zero of energy at $V_{\mathrm{MEP}}(s)$ and with all rotational symmetry numbers set to unity. To include quantum tunneling effects for motion along the reaction coordinate, CVT rate constants were multiplied by a transmission coefficient. In particular, we employed the small curvature tunneling (SCT) method, based on the centrifugal-dominant small-curvature semi-classical adiabatic ground-state approximation, to calculate the transmission coefficient. The rotational partition functions were calculated classically, and the vibrational modes were treated as quantum-mechanically separable harmonic oscillators. The rate constant calculations were carried out with POLYRATE 9.3 program (Steckler et al., 2002).

3. Results and discussion

The reliability of the theoretical calculations was confirmed firstly. The geometries and vibrational frequencies of $CH_3COOCH_2CH_3$ and CH_3CHO were calculated at the B3LYP/6-31G(d,p) level. The results show good consistency with the corresponding experimental values, and the relative deviation remains within 1.0% for the geometrical parameters and 4.0% for the vibrational frequencies (Kuchitsu, 1998; Hollenstien and Gunthard, 1971). For the reaction of $C_4H_{10} + OH \rightarrow C_4H_9 + H_2O$, the reaction enthalpy of −16.15 kcal mol^{-1} obtained at the CCSD(T)/6-31G(d)+CF level and 0 K agrees well with the experimental value of −18.55 kcal mol^{-1} (IUPAC, 2006).

As shown in Fig. 1, there are four geometric conformers resulting from the internal rotation of the $O{-}C_4$ and $C_1{-}C_2$ bonds for methyl propionate. Structure A is 8.21, 1.28 and 9.40 kcal mol^{-1} more stable than structures B, C and D. So throughout this paper, methyl propionate denotes structure A.