Theoretical study for OH radical-initiated atmospheric oxidation of ethyl acrylate

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HIGHLIGHTS

- Oxidation mechanism for EA with OH radicals was investigated for the first time.
- Rice–Ramsperger–Kassel–Marcus theory was used to predict the rate constants.
- $k_{(EA+OH)} = (1.71 \times 10^{-12})\exp(805.42/T)$ cm^3 molecule^{-1} s^{-1}.
- The atmospheric lifetime determined by OH radicals is about 16.2 h.

ARTICLE INFO

ABSTRACT

OH radical-initiated atmospheric oxidation of ethyl acrylate (ethyl 2-propenoate, EA) has been investigated by performing density functional theory (DFT) calculations. Optimizations of the reactants, intermediates, transition states and products were carried out at the MPWB1K/6-31+G(d,p) level. Single-point energy calculations were performed at the MPWB1K/6-311+G(3df,2p) level of theory. The detailed oxidation mechanism was presented and discussed. The results show that the OH addition is more energetically favorable than the H abstraction. Rice–Ramsperger–Kassel–Marcus (RRKM) theory was used to predict the rate constants over the possible atmospheric temperature range of 180–370 K. The Arrhenius expression adequately describes the total rate constant: $k_{(EA+OH)} = (1.71 \times 10^{-12})\exp(805.42/T)$ cm^3 molecule^{-1} s^{-1}. At 298 K, the atmospheric lifetime of ethyl acrylate determined by OH radicals is about 16.2 h. In order to find out the effect of alkyl substitution on the reaction activity, rate constants for the reactions of methyl acrylate, methyl methacrylate and butyl acrylate with OH radicals were also discussed. Calculation results show that the reaction activity may increase with the increased electron-donating substitution for electrophilic addition reaction.

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1. Introduction

As an important kind of unsaturated oxygenated volatile organic compounds (OVOCs), α,β-unsaturated esters have been widely used in the production of pesticides, polymers, resins and cleaning products (Graedel, 1978). They are directly emitted into the atmosphere from biogenic sources (mainly vegetation) and anthropogenic sources (fossil fuel combustion, solvent use, adhesives, etc.). Many kinds of α,β-unsaturated esters including ethyl acrylate, methyl acrylate, methyl methacrylate and butyl acrylate have been detected in ambient air (Pankow et al., 2003).

Ethyl acrylate (CH$_2$=CHC(O)OCH$_2$CH$_3$, ethyl 2-propenoate, EA) is an important monomer that can be used extensively in the manufacture of various polymers and copolymers including resins,

plastics, rubber, and denture material (Hazardous Substance Fact Sheet). Just in China, about 100 thousand tons of ethyl acrylate was produced in 2011. Ethyl acrylate is toxic, and may cause irritation and burn of eyes and skin. Exposure to excessive vapor concentration can also cause drowsiness accompanied by nausea, headache, or extreme irritation of the respiratory tract. Ethyl acrylate can be released into the environment in fugitive and stack emission or in wastewater during its production and use (HSDB). Due to its high vapor pressure (28.8 mmHg at 293 K), ethyl acrylate exists mainly in the gas phase under the general atmospheric conditions. With growing use of ethyl acrylate, the atmospheric concentration increases as well. It can undergo transformation or degradation in the atmosphere, which may significantly contribute to the formation of ozone and other secondary photo oxidants (Mellouki et al., 2003). Therefore, it is necessary to study its transformation mechanism in order to assess its potential impact to the atmosphere.

When released into the atmosphere, the removal or transformation of ethyl acrylate includes photolysis, wet and dry deposition, and oxidation reactions with OH, NO_3 radicals, O_3 molecules and Cl atoms. Photolysis is expected to be a minor degradation process for the α,β-unsaturated esters, since they do not absorb radiation at actinic wavelengths. Due to the high volatility and sparing solubility in water, dry and wet deposition also are of minor importance atmospheric loss processes. Reaction with Cl atoms is considered to be significant in certain locations during certain times of the year (Martín Porrero et al., 2010). Among the various oxidants, OH radicals play the most central role in determining the oxidation power of the atmosphere. The reaction of ethyl acrylate with OH radicals is considered to be a dominant removal process.

Limited experimental studies have been performed concerning the tropospheric oxidation of ethyl acrylate. In 2006, the rate coefficients for the gas-phase reaction of ethyl acrylate with OH radicals were determined firstly by Teruel et al. over the temperature range of 253–374 K, which was $k = (1.70 \pm 0.4) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K (Teruela et al., 2006). Wang et al. reported the rate constant for the gas-phase reaction of ethyl acrylate with NO_3 radicals at 298 ± 1 K (Wang et al., 2010). In 2010, (Bernard et al., 2010) experimentally investigated the kinetics and products of gas-phase reaction of ethyl acrylate with ozone. The rate constant was $(1.3 \pm 0.1) \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} at 294 ± 2 K and 760 Torr, and the major reaction products were ethyl glyoxylate and formaldehyde. Gas phase reaction of ethyl acrylate with Cl atom has been carried out in a static Teflon reactor at 298 ± 2 K and 1 atm. The obtained rate coefficient of ethyl acrylate with Cl is $(1.82 \pm 0.13) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (Martín Porrero et al., 2010).

However, due to lack of efficient detection schemes for radical intermediate species, the detailed mechanism for the oxidation reaction of ethyl acrylate has not been fully obtained. Quantum calculation is especially suitable to find out favorable reaction pathways and sites. The potential energy surface is useful to explain the experimentally observed degradation products, thermochemical properties, and rate coefficients. In this paper, detailed kinetic and mechanistic studies on OH radical-initiated oxidation degradation of ethyl acrylate were carried out.

2. Computational method

Geometries of the reactants, intermediates, transition states and products for ethyl acrylate + OH reaction system were optimized at the MPWB1K (Zhao and Truhlar, 2004) level with a standard 6-31+G(d,p) basis set. The harmonic vibrational frequencies were also calculated at the same level to verify the nature of the stationary points, the zero-point energy (ZPE), and the thermal contribution to the free energy of activation. The connection of transition state structure between designated reactants and products has been confirmed in each case by intrinsic reaction coordinate (IRC) calculations (Gonzalez and Schlegel, 1989, 1990). Based on the optimized geometries, a more flexible basis set, 6-311+G(3df,2p) was employed to calculate the single point energies of various species. The potential energy surfaces (PESs) were constructed at the MPWB1K/6-311+G(3df,2p)//MPWB1K/6-31+G(d,p) level including zero-point vibration energy (ZPVE) correction. All calculations were performed using the Gaussian 03 software package (Frisch et al., 2003).

By means of the MESMER program (Glowacki et al., 2012), the rates constants of the crucial elementary reactions were deduced by using Rice–Ramsperger–Kassel–Marcus (RRKM) theory (Robinson and Holbrook, 1972). The RRKM rate constant is given by:

$$k(E) = \frac{W(E)}{h\rho(E)} \tag{1}$$

where $W(E)$ is the rovibrational sum of states at the transition state, $\rho(E)$ is density of states of reactants, and h is Planck's constant. Then, canonical rate constant $k(T)$ is determined by using the usual equation:

$$k(T) = \frac{1}{QT} \int k(E)\rho(E)\exp(-\beta E)\,dE \tag{2}$$

where $Q(T)$ is the reactant partition function.

3. Results and discussion

The reliability of the theoretical calculations was confirmed. The geometries and vibrational frequencies of $CH_3(CH_2)_3CH_3$, HCHO and H_2O were calculated at the MPWB1K/6-31+G(d,p) level. The results show reasonable accordance with the corresponding experimental values, and the relative deviation remains within 2.0% for the geometrical parameters and 6.0% for the vibrational frequencies (CCCBDB). For the reaction of $CH_3CH_2CH_2CH_3 +$ OH → $CH_3CH_2CH_2CH_2 + H_2O$, the reaction enthalpy obtained at the MPWB1K/6-311+G(3df,2p)//MPWB1K/6-31+G(d,p) level and 0 K is -15.86 kcal mol^{-1}, which agrees well with the experimental value of -17.30 kcal mol^{-1} (IUPAC, 2008).

Due to the internal rotation of the O_2—C_4 and C_4—C_5 bonds of ethyl acrylate, four geometric conformers are considered as shown in Fig. 1. Structure A is more stable (0.44, 8.12 and 8.95 kcal mol^{-1}) than structures B, C and D. So throughout this paper, structure A was chosen for the investigation.

3.1. OH radical-initiated reaction

The OH radical-initiated reaction schemes embedded with the potential barriers and reaction heats were depicted in Fig. 2(a). There exist C—H and C=C bonds in the molecular structure of ethyl acrylate. Thus, OH addition to C=C bond and H abstraction from the C—H bonds are possible pathways for the reaction of ethyl acrylate with OH radicals. For convenience, the five carbon atoms in ethyl acrylate are labeled as C_1, C_2, C_3, C_4 and C_5, as shown in Fig. 2(a).

Atoms C_1 and C_2 on the double bond are inequitable, with the charge of -0.333 and 0.240, respectively. Therefore, OH radical attacks C=C bond through two different channels, as seen in Fig. 2(a). The two addition reactions proceed via the formation of the same van der Waals complex (named vdW1 or vdW2). As see in Fig. 2(b), the bond lengths of C_1–O_3, C_2–O_3 in vdW1 (vdW2) are 2.667 and 2.665 Å, respectively. This complex possesses 2.48 kcal mol^{-1} energy lower than reactants. Then, intermediates IM1 and IM2 are formed via transition states TS1 and TS2, respectively. The energy barriers and exothermic heats of the two pathways are 1.97, 0.45 and 26.71, 30.85 kcal mol^{-1}, respectively.

There are five different types of hydrogen atoms in the ethyl acrylate molecule. So, five possible H abstraction channels were identified: H abstractions from the C_1–H_1, C_1–H_2, C_2–H_3, C_4–H_4 and C_5–H_6 bonds. Thus, five transition states, TS3, TS4, TS5, TS6 and TS7, were located, as seen in Fig. 2(a). They were identified with one and only one negative eigenvalue of the Hessian matrix and, therefore, one imaginary frequency. The geometrical structures of the five transition states are shown in Fig. 2(b). After the H abstraction, open-shell activated radicals IM3, IM4, IM5, IM6 and IM7 are produced. All the H abstraction processes are exothermic. From Fig. 2(a), we can see that the H abstraction from the —CH_2— group is the most energetically favorable because of the low energy barrier (~3.16 kcal mol^{-1}) and high exothermicity (~16.34 kcal mol^{-1}). There exist obvious hydrogen bonds in the pre-reaction vdW complex vdW6 (H_9—O_1) and transition state TS6 (H_9—O_1), which have the bond length of 1.885 Å and 2.214 Å,