Computational and Theoretical Chemistry 1091 (2016) 99–106

Contents lists available at ScienceDirect

Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc

Theoretical study on the mechanisms and kinetics of Cl-initiated oxidation of methyl acrylate

Shiqing Zhang, Haijie Cao, Xin Li, Jianfei Sun, Maoxia He *

Environment Research Institute, Shandong University, Jinan 250100, PR China

ARTICLE INFO

Article history:
Received 6 June 2016
Received in revised form 8 July 2016
Accepted 8 July 2016
Available online 12 July 2016

Keywords:
Methyl acrylate
Cl atoms
Mechanisms
Kinetics
Products

ABSTRACT

The atmospheric oxidation mechanism and kinetics of Cl with methyl acrylate are investigated in this study. The mechanisms of MA with Cl atoms have been obtained in detail at the M06-2X/6-311++G (3df, 2p)//M06-2X/6-31+G(d, p) level of theory. The reaction initiates with two kinds of reaction pathways: Cl-addition and H-abstraction. In general, Cl atoms attacking to terminal carbon (the pathway producing IM1) is more favorable. Hydrogen abstraction from the —CH_3 group also plays an important role. Besides, the kinetic results are determined by MESMER program on the basis of Rice–Ramsperger–Kassel–Marcus (RRKM) theory. The calculated results show that the addition reactions predominate the initial reaction under atmospheric condition and the calculated total rate constant is 1.66×10^{-10} cm^3 molecule^{-1} s^{-1} at 298 K and 760 Torr.

1. Introduction

Oxygenated volatile organic compounds (OVOCs) are very important in atmospheric chemistry [1]. They derived from the anthropogenic and biogenic sources [2]. As a kind of OVOCs, esters are commonly used as diesel fuel or components [3]. In the ambient air, many kinds of α,β-unsaturated esters have been detected such as methyl acrylate (MA), methyl methacrylate (MMA) and ethyl acrylate (EA) [4]. They can be emitted from the manufacture of plastics and the electronic components [5]. In addition, certain ethers used as automobile fuel additives can form the oxidation products and acrylates in the atmosphere [6,7]. These compounds are volatile and sometimes toxic, causing a series of environmental problems that cannot be ignored especially in industrial areas [8]. Furthermore, α,β-unsaturated esters are used in industrial applications as important monomers [2]. The carbonyl carbon and the vinyl groups will make up a conjugated system. Because of this special structure, unsaturated OVOCs are highly reactive. Once released into the troposphere, these compounds undergo transformation or degradation by reactions with Cl atoms or other oxidants such as OH and NO_3 radicals, O_3 molecules. Debasish et al. [9] have studied the kinetics and mechanisms of the vinyl acetate with OH radical in the troposphere. The researches of OH and ozone atmospheric reactions with EA have already been investigated by Sun et al. [10,11]. These reactions are evidenced to produce some secondary photo-oxidants in polluted areas [12]. Also, some previous researches have studied the reactions of Cl atoms with the OVOCs [13–15].

For acrylate esters, the reaction with OH radical will be a predominant loss process in the atmosphere [16,17]. However, Atkinson et al. pointed out that the reactions with Cl atoms are important in the atmospheric chemistry and sometimes they would be faster relative to the OH-participated reactions [18]. In addition, a study has reported that the photolytic degradation of acrylate esters could be negligible [19]. And hence, it is important to study the reactions of the acrylate esters with Cl atoms.

According to Spicer et al., the maximum concentration of Cl atoms can be 1×10^5 atoms cm^{-3} in some seaside regions [20]. Therefore, in these areas the degradation of the unsaturated esters initiated by Cl atoms are very important on condition that other homogeneous loss ways are slow and sometimes negligible [21]. In some industrial areas, the concentrations of chlorides have been detected as high as 40–200 ppm [22]. In polluted coastal regions, nitryl chloride ($ClNO_2$) can be an important source of atomic Cl [23]. In addition, the studies of Cl chemistry are becoming important in the continental areas which are proved by Thornton et al. [24].

MA ($CH_2{=}CHC(O)OCH_3$) is an important kind of OVOCs and α,β-unsaturated esters which has been used in many industrial applications [2]. MA is toxic and harmful to our eyes and skin. Like other OVOCs, MA can undergo reactions with some oxidants that are useful for its transformation or degradation in the atmosphere. Also, these reactions can form the secondary photo-oxidants. In

---

* Corresponding author.
E-mail address: hemaox@sdu.edu.cn (M. He).

http://dx.doi.org/10.1016/j.comptc.2016.07.008
2210-271X/

order to obtain its potential influence on the environment, we should study its transformation mechanisms and kinetics. However, the information of kinetic and products is especially scarce. Most of the studies of Cl atoms with MA are performed experimentally. The previous study [21] has obtained the rate constant for reaction of Cl with MA, and the total rate constant is $(1.71 \pm 0.13) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K and 760 Torr. Temperature-dependent rate constant for the reaction of Cl atoms with MA at atmospheric pressure also has been studied [8]. The results have shown negative temperature dependence. Besides, HCHO, $CH_3OC(O)CHO$, $HC(O)CH_2Cl$ and $CH_3OC(O)C(O)CH_2Cl$ are the major products for the atmospheric oxidation of MA in an experimental study [25]. However, the detailed mechanisms for the reactions of MA with Cl atoms have not been fully obtained at present. Hence, the quantum calculation will be chosen to prove the experimental observations, which is useful to get a particular knowledge of the oxidation pathways. In this study, mechanisms for Cl-initiated oxidation reaction of MA are postulated in detail, and whole reactions are treated step by step. Furthermore, the rate constants for the crucial elementary reactions (R1-R7) are determined.

2. Computational methods

All the calculations reported in this study are based on the density functional theory (DFT) [26] and carried out employing Gaussian 09 program [27]. All geometrical structures of the reactants (R), intermediates (IM), transition states (TS), pre-complexes, and products (P) in this study are optimized using density functional M06-2X method with 6-31+G(d, p) basis set [28]. The M06-2X is developed from the M06 family of local (M06-L) and hybrid (M06) meta-GGA functional by Zhao and Truhlar [29]. The method has been employed for the kinetic and thermodynamic theoretical calculations in previous studies [30–32] and it has shown the promising performance. The zero point vibrational energies (ZPVEs), the Gibbs free energy, the Enthalpy, the Entropy and the harmonic vibrational frequencies are obtained at the same level. In addition, the single-point energy calculations are determined at the M06-2X/6-311++G(3df, 2p) level to obtain accurate energies. The calculations of rate constants for the primary reactions are determined using MESMER program [33], on the basis of the thermochemical results and the Rice–Ramsperger–Kassel–Marcus (RRKM) theory [34]. This theory has been successfully employed to study other similar reaction [10].

3. Results and discussion

The optimized geometries and atom numbering of MA are shown in Fig. 1. Apparently, MA contains C=C double bond, —C=O bond and five kinds of C—H bonds. Hence, the primary reactions of MA with Cl atoms contain three possible pathways: Cl addition to C_1 and C_2, Cl addition to —C=O bond and five H-abstractions. However, the previous study suggested that reaction of Cl atoms addition to the —C=O bond suffers very high barrier height and is hard to take place [35]. Therefore, the channel of Cl addition to the —C=O bond will be ignored and other pathways will be studied here step by step.

In this study, the energies of MA and Cl are set as 0.0 kcal mol^{-1} and all of the calculated energies for primary reactions are relative to that of MA + Cl. The Enthalpy change, Entropy changes are respectively marked as ΔH^*, $\Delta_r H$, ΔS^* and $\Delta_r S$ and they are shown in supporting information Table 1s. The energy barrier and reaction heat in terms of gibbs free energies are labeled as ΔG^* and $\Delta_r G$, respectively.

3.1. The primary reactions of MA with Cl atoms

3.1.1. Addition reactions

The C=C double bond has a π system and the Cl atoms has electrophilic nature, so the initial Cl addition reaction to MA is performed as the electrophilic addition. As shown in Fig. 2, Cl atoms can attack to C_1 (the terminal carbon) and C_2, yielding two different radical intermediates, IM1 and IM2 which are 17.69 and 9.39 kcal mol^{-1} lower than the energy of the separated reactants MA + Cl respectively. Both the formation of IM1 and IM2 are exothermic reaction. Further, the results show that reaction of Cl addition to the terminal carbon releases more energy than that of Cl addition to C_2. IM1 is a thermodynamically controlled product. In addition, both of IM1 and IM2 are formed via barrierless reactions. And they will be kinetically controlled products.

3.1.2. H abstraction pathways

As shown in Fig. 1, the charge distributions of H-atoms in MA are 0.190, 0.164, 0.174, 0.173, 0.173, 0.163 for H_1-H_6, respectively. Because of the different charge distribution of H-atoms, there are five kinds of H atoms (H_1, H_2, H_3, and $H_4 = H_5$, H_6) for MA, and the channels R3-R7 are for five H abstractions. All of these reactions will form an intermediate (IM3-IM7) and HCl molecule (Fig. 2).

In MA, there are two kinds of H-atoms linked on C_1 (H_1 and H_2 atoms) and they have different chemical environment. The H_1 atom can be abstracted through the transition state TS3 with an energy barrier of 11.36 kcal mol^{-1}. Then, the radical intermediate IM3 and HCl molecule are formed. The energy of (IM3 + HCl) is 6.77 kcal mol^{-1} higher than that of MA + Cl. H_2 atom can be abstracted by Cl atoms to form the radical intermediate IM4 and HCl molecule as well as H_1 atom. The transition state TS4 and products (IM3 + HCl) are 14.50 and 5.78 kcal mol^{-1} higher than that of separated reactants respectively.

There is only one H atom (H_3) located at C_2, which is one of the C=C double bonds as well as near the carbonyl group. And it is hard to be abstracted by Cl atoms. Through transition state TS5 (17.01 kcal mol^{-1}), the radical intermediate IM5 and HCl molecule are formed from the reaction of H_3 abstracted by Cl.

In addition, there are three H atoms (H_4, H_5, H_6) situated in C_4. H_4 and H_5 atoms have the same chemical environment and they are different from H_6 atom. Hence, we chose H_4 and H_6 atoms to study the H-abstraction reactions of C_4. For the reaction of Cl abstracting H_4 atom, the radical intermediate IM6 and HCl molecule are formed via the transition state TS6, which is 5.02 kcal mol^{-1} higher than that of MA and Cl. For Cl abstraction H_6 atom, IM7 and HCl are produced via TS7, which need an energy barrier of 6.94 kcal mol^{-1}. The reaction heat of this reaction is −1.74 kcal mol^{-1}.

MA + Cl	→	IM1	R1
	→	IM2	R2
	→	TS3 → IM3 + HCl	R3
	→	TS4 → IM4 + HCl	R4
	→	TS5 → IM5 + HCl	R5
	→	TS6 → IM6 + HCl	R6
	→	TS7 → IM7 + HCl	R7

Compared all the H-atom abstraction channels, we can know that the energy barrier is: R6 < R7 < R3 < R4 < R5. The H atoms lied on methyl (H_4 and H_6) are easy to be abstracted by Cl because these reactions face relatively lower energy barrier. However, due to higher energy barrier, the H-abstraction from C_2 is hard to occur.