

Research Article

Mechanism of Chlorination Process: From Propanoic Acid to α -Chloropropanoic Acid and Byproducts Using Propanoic Anhydride as Catalyst

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Received 25 February 2017; Accepted 7 May 2017; Published 4 June 2017

Academic Editor: Gulaim A. Seisenbaeva

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This article reports on findings regarding the mechanism of chlorination process. In this experiment, propanoic acid was chlorinated to α -chloropropanoic acid in a lab-scale glass tube reactor operating at 130°C. Propanoic anhydride and concentrated sulfuric acid were, respectively, used as the catalyst and the promoter. This experiment adopted the DFT method to calculate the activation energy of routes for the synthesis α -chloropropanoic acid, β -chloropropanoic acid, α,α -dichloropropanoic acid, and α,β -dichloropropanoic acid. The results showed that the main route of α -chloropropanoic acid was formed through an ionic mechanism when propanoic anhydride was used as the catalytic agent. Activation energy of 1-propen-1-ol,1-chloro-, which was formed from 1-prop-anol,1-chloro-, was the highest in the process of ionic mechanism. In addition, α,α -dichloropropanoic acid was formed via a consecutive ionic chlorination path from α -chloropropanoic acid. β -Chloropropanoic acid was produced from propanoic acid through a chlorination radical mechanism. α,β -Dichloropropanoic acid was formed via a consecutive radical chlorination path.

1. Introduction

α -Chloropropanoic acid, as a kind of active organic chemical, has been widely used to produce pesticides, dyes, chemicals of agriculture and forestry, intermediates, and so forth. It plays an important role in the fine chemical industry. Due to the existence of a chlorine atom in the α -chloropropanoic acid's molecular structure, its acidic density and reactivity are stronger than those of propanoic acid, which is more active in chemical reactions [1–4].

Sioli et al. [5] proposed the acid-catalyzed enolization of ionic mechanism for the first time to explore the synthesis of α -chloropropanoic acid. Paatero et al. [6] found that acid catalysis was a process of autocatalysis when using chlorosulfonic acid as an enolizing agent. Salmi et al. [7, 8] and Mäki-Arvela et al. [9] identified an autocatalysis effect. They found that the monochloropropanoic acid created in the reaction was much stronger than the propanoic acid [10], which led to an increasing rate of acid catalysis and autocatalysis. The autocatalytic kinetic was explained by a

reaction involving the acid-catalyzed enolization of the key intermediate, propanoyl chloride, as a rate-determining step.

Ogata et al. [11] and Ham et al. [12] found that the generation of β -chloropropanoic acid was by radical chlorination in the α -chloropropanoic acid synthesis process. Paatero et al. [6] identified that the formation route of α,α -dichloropropanoic acid was the same as α -chloropropanoic acid formation, the parallel acid-catalyzed enolization mechanism. Mäki-Arvela et al. [10] also found that α,α -dichloropropanoic acid generation has two routes: the ionic mechanism and the radical mechanism. There exists a competition between these two mechanisms. α,β -Dichloropropanoic acid was formed through further chlorination of α -chloropropanoic acid.

However, the reaction mechanisms of byproducts, for instance, the α,α -dichloropropanoic acid, have received different opinions. Thus, this article aims to report on findings on the reaction mechanism of chlorination products through experimenting with propanoic acid chlorinated by using the density function method with Dmol³ program of Materials

Studio 5.5. The results could contribute to production optimization of α -chloropropanoic acid.

2. Experimental and Calculation Section

2.1. Experimental. Propanoic acid chlorination was carried out in a homemade glass tube equipped with a magnetic stirring apparatus and an oil bath heater with a temperature control. Chlorine gas was dispersed into the reaction mixture which was metered by a rotameter. A reflux condenser equipped with low temperature cooling circulating pump was placed on the top of the reactor. The gaseous compounds passed through water, sodium bicarbonate solution, and concentrated sodium hydroxide solution before being released to the air.

The propanoic acid to be chlorinated was placed in the reaction vessel. A slightly excess chlorine feed was introduced, and the liquid phased was heated to the desired reaction temperature. A certain amount of propanoic anhydride was added. Samples of the liquid phase were analyzed with gas chromatograph after esterification [10].

2.2. Calculation Methods. Density functional theory method quantum chemistry calculation was adopted and the calculations were performed by using the Dmol³ program mounted on Materials Studio 5.5 package. All the reactants and products in the chlorination reaction were optimized and their stable structures were obtained at the same time. All transition states of the reactions were trialed and searched carefully by using an LST/QST method, getting the primitive activation energy and the heat of reaction. The nonlocal exchange and correlation energies were calculated by the PW91 function of the generalized gradient approximation (GGA) [13] and a double numerical plus polarization (DNP) basis set in the level of All Electron. The convergence criteria included threshold values of 1×10^{-5} Hartree, 0.02 Hartree per nm, and 0.0005 nm for energy, force, and displacement convergence, respectively, while the self-consistent field (SCF) density convergence threshold value was specified as 1×10^{-6} Hartree. Fermi smearing of 0.005 Hartree was employed to improve the computational performance, and the solvent effect was also considered during the calculations. The geometries of all stationary points were optimized at this level.

3. Results and Discussion

3.1. The Experimental Results. The experiment first investigated the effect of propanoic acid catalytic chlorine (see Figure 1) in the condition of 15 ml propanoic acid, 5 ml propanoic anhydride, 130°C reaction temperature, and 40 ml/min chlorine flow rate with micro excess. The generation of α -chloropropanoic acid was little in the first 30 min and increased rapidly during the period from 30 min to 150 min. Its generation did not increase obviously thereafter. The generation of β -chloropropanoic acid increased steadily in the first 150 min but increased slowly from 150 min to 360 min. The generation of α,α -dichloropropanoic acid increased quite

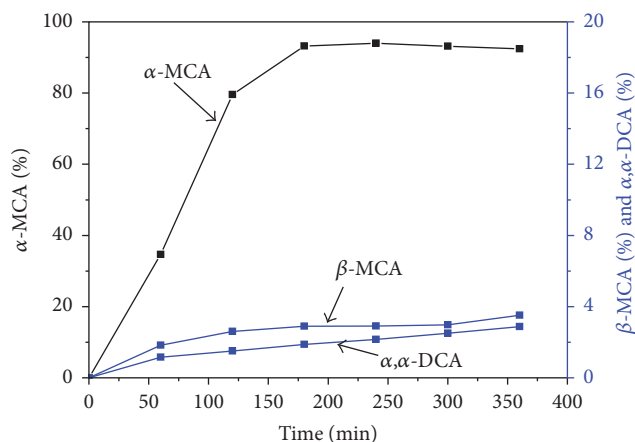


FIGURE 1: The reaction products change over time at 130°C.

slowly before 250 min and increased rapidly in the later reaction.

In order to verify the catalytic principle, 0.4 ml concentrated sulfuric acid was added to propanoic anhydride catalytic chlorination to observe the effect of the chlorination reaction, compared with the control experiment. Chloride products were analyzed by gas chromatography (Table 1). It was found that the generation of α -chloropropanoic acid increased obviously, while the generation of both β -chloropropanoic acid and α,α -dichloropropanoic acid reduced after concentrated sulfuric acid was added. Also, the generation of α -chloropropanoic acid (Table 1, Entry α -MCA (%)) increased rapidly in the first 90 min, increased slowly from 90 min to 150 min, and barely increased from 150 min to 180 min. The generation of β -chloropropanoic acid (Table 1, Entry β -MCA (%)) shrank with time. The generation of α,α -dichloropropanoic acid (Table 1, Entry α,α -DCA (%)) increased in the first 30 min but reduced from 30 min to 180 min.

3.2. Synthesis Mechanism of α -Chloropropanoic Acid. In order to investigate the formation route of α -chloropropanoic acid, two possible reaction paths were constructed: the radical chlorination mechanism and ionic chlorination mechanism (Scheme 1). Path 1 is the formation route of α -chloropropanoic acid via radical chlorination mechanism (Scheme 1; see (1)). Path 2 is the formation route of α -chloropropanoic acid via ionic chlorination mechanism (Scheme 1; see (2)–(6)).

The configurations of reactants and products were built and the geometry structure was optimized. Transition states were investigated and calculated on the basis of reactants and products. Each reaction transition state was derived from the potential energy surface at the highest point of the potential energy corresponding to the configuration. Frequency analysis showed that these configurations were the only virtual frequency. Energy of reactants, products, and transition states to relevant primitives and the corresponding virtual frequency of the transition state are presented (Table 2). At the same time, energy potential diagrams of the

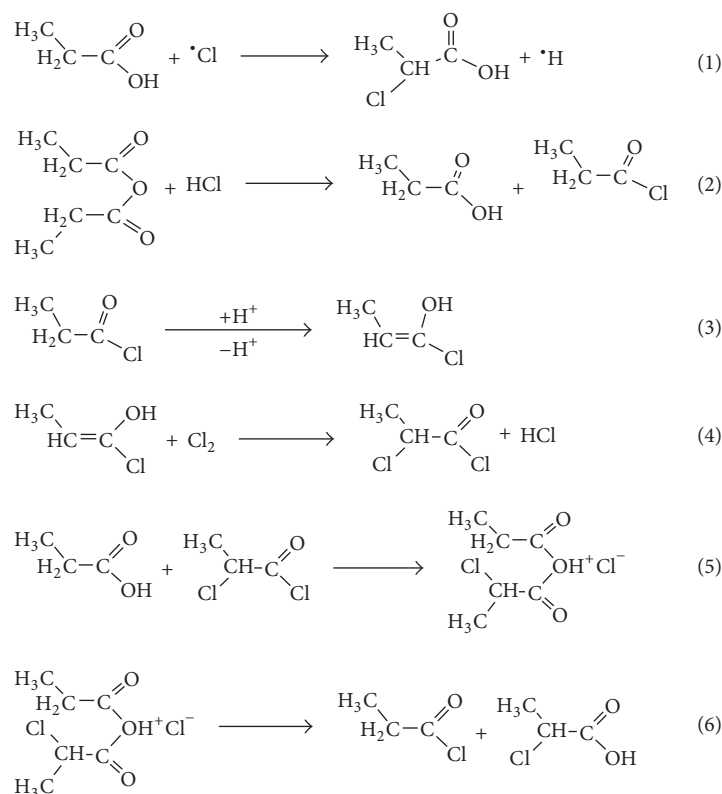
SCHEME 1: Paths of the generated α -chloropropanoic acid.

TABLE 1: Different chloride products change over time without concentrated sulfuric acid and joining concentrated sulfuric acid.

Catalyst	T (min)	Propanoic acid (%)	α -MCA (%)	β -MCA (%)	α,α -DCA (%)
20 mol% propanoic anhydride	30	80.05	18.23	1.24	0.47
	60	62.56	34.63	1.83	0.98
	90	39.74	56.73	2.11	1.42
	120	11.13	84.84	2.47	1.56
	150	5.80	89.79	2.63	1.78
	180	0.51	94.57	2.91	2.01
20 mol% propanoic acid anhydride + concentrated sulfuric acid	30	46.52	52.18	0.59	0.71
	60	30.66	67.71	0.82	0.81
	90	13.16	85.04	0.93	0.87
	120	5.8	92.18	1.04	0.98
	150	3.23	94.53	1.18	1.06
	180	0.41	97.22	1.24	1.13

primitive reactions with corresponding reactants, transition states, and products of configuration are shown in Figure 2.

The formation of α -chloropropanoic acid via ionic chlorination mechanism is as follows. First, propanoic anhydride conducted initiation (Scheme 1; see (2)) and formed propanoyl chloride. Its reaction activation energy was 12.54 kJ/mol. Propanoyl chloride then conducted enolization (Scheme 1; see (3)) and formed 1-propen-1-ol, 1-chloro, and the corresponding primitive activation energy was 125.73 kJ/mol. Since then, the double bond in 1-propen-1-ol, 1-chloro

was apt to react with chlorine (Scheme 1; see (4)) and formed α -chloropropanoyl chloride, and the corresponding primitive activation energy was 20.11 kJ/mol. Finally, the OH and Cl exchange reaction generated α -chloropropanoic acid (Scheme 1; see (5) and (6)) and its activation energy was 85.61 kJ/mol and 90.48 kJ/mol. Therefore, reaction (2) was the catalyst initiation reaction among whole reactions (2)–(6) and propanoic acid anhydride formed a real catalyst, propanoyl chloride. The whole reaction process became an acid catalytic reaction once propanoyl chloride was formed.

TABLE 2: Possible elementary reactions involved in α -chloropropanoic acid and byproducts synthesis together with the activation energies (Ea) and reaction energies (ΔH).

Step	Chemical reaction	Frequency (cm ⁻¹)	Ea (kJ·mol ⁻¹)	ΔH (kJ·mol ⁻¹)
(1)	$C_2H_5COOH + \cdot Cl \rightarrow H^+ + CH_3CHClCOOH$	-237.61	158.37	131.50
(2)	$(C_2H_5CO)_2O + HCl \rightarrow C_2H_5COOH + C_2H_5COCl$	-118.79	12.54	-9.68
(3)	$C_2H_5COCl + H^+ \rightarrow H^+ + CH_3CHClOH$	-117.24	125.73	117.19
(4)	$CH_3C_2HClOH + Cl_2 \rightarrow HCl + C_2H_4ClCOCl$	-48.63	20.11	-170.74
(5)	$C_2H_4ClCOCl + C_2H_5COOH \rightarrow C_6H_{10}O_3Cl_2$	-161.81	85.61	19.05
(6)	$C_6H_{10}O_3Cl_2 \rightarrow C_2H_5COCl + CH_3CHClCOOH$	-138.82	90.48	-116.71
(7)	$C_2H_5COOH + \cdot Cl \rightarrow H^+ + CH_2ClCH_2COOH$	-343.25	217.04	146.69
(8)	$CH_3C_2HClOH + Cl_2 \rightarrow HCl + CH_2ClCH_2COCl$	-294.33	110.27	-187.88
(9)	$CH_2ClCH_2COCl + C_2H_5COOH \rightarrow C_6H_{10}O_3Cl_2$	-121.03	188.14	106.79
(10)	$C_6H_{10}O_3Cl_2 \rightarrow C_2H_5COCl + CH_2ClCH_2COOH$	-208.36	34.54	-122.72
(11)	$CH_3CHClCOOH + \cdot Cl \rightarrow H^+ + CH_3CCl_2COOH$	-758.10	162.64	134.13
(12)	$CH_3CHClCOOH + \cdot Cl \rightarrow H^+ + CH_2ClCHClCOOH$	-486.96	180.08	138.43
(13)	$CH_2ClCH_2COOH + \cdot Cl \rightarrow H^+ + CH_2ClCHClCOOH$	-887.32	178.87	153.22
(14)	$CH_3CHClCOCl + H^+ \rightarrow H^+ + CH_3CClCClOH$	-1103.93	130.81	117.22
(15)	$CH_3CClCClOH + Cl_2 \rightarrow HCl + CH_3CCl_2COCl$	-84.36	21.99	-129.19
(16)	$CH_3CCl_2COCl + C_2H_5COOH \rightarrow C_6H_9O_3Cl_3$	-69.22	82.61	-168.57
(17)	$C_6H_9O_3Cl_3 \rightarrow CH_3CCl_2COOH + C_2H_5COCl$	-365.41	109.73	-95.67

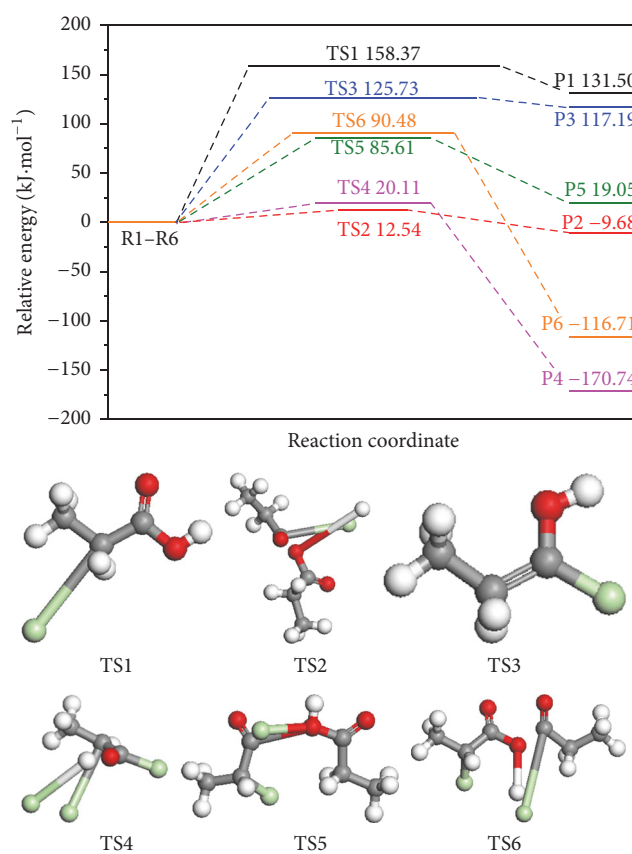
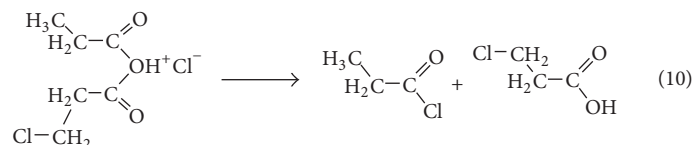
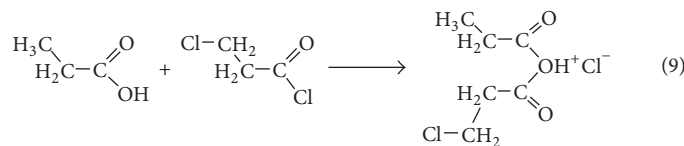
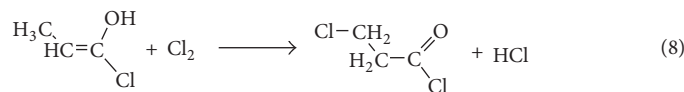
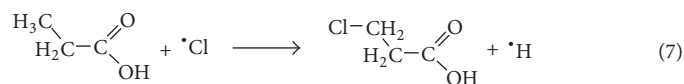


FIGURE 2: Potential energy diagram of α -chloropropanoic acid synthesis together with the initial states, transition states, and final states.



SCHEME 2: Radical chlorination mechanism of byproducts.

More importantly, the acidity of α -chloropropanoic acid was stronger than that of propanoic acid, so the acid catalytic reaction was accelerated.

The activation energy 125.73 kJ/mol (Scheme 1; see (3)) was the highest as the rate-determining step after propanoyl chloride was formed. It is consistent with the results of Paatero. The results also showed that the formation rate of α -chloropropanoic acid was slow at the beginning and was rapid in the middle of the reaction. The reason for it could be that catalyst initiation reaction was slow, and the activation energy of the whole process would reduce once propanoyl chloride was formed. Meanwhile, the rate of acid catalysis and autocatalysis (Scheme 1; see (3)) was accelerated due to the fact that the acidity of α -chloropropanoic acid was stronger than that of propanoic acid. Thus, the generation speed of α -chloropropanoic acid was accelerated. In addition, the generation of α -chloropropanoic acid increased significantly when concentrated sulfuric acid was added. The added H^+ in the reaction system promoted the progress of acid catalysis and autocatalysis (Scheme 1; see (3)). In turn, it led to the result that the reaction was conducted toward the generation of α -chloropropanoic acid. Therefore, it can be drawn from the theoretical calculation and experimental results that the whole process became an acid catalytic reaction when propanoyl chloride was formed. The generation of α -chloropropanoic acid could be accelerated as long as propanoyl chloride acid-catalyzed enolization (Scheme 1; see (3)) was expedited. It could also inhibit the generation of β -chloropropanoic acid and α,α -dichloropropanoic acid.

3.3. Synthesis Ionic Chlorination Mechanism of β -Chloropropanoic Acid. In order to investigate the formation route of β -chloropropanoic acid, two possible reaction paths were constructed: the radical chlorination mechanism and ionic chlorination mechanism (Scheme 2, Figure 3). Path 1 is the formation route of β -chloropropanoic acid via radical chlorination mechanism (Scheme 2; see (7)). Path 2 is the

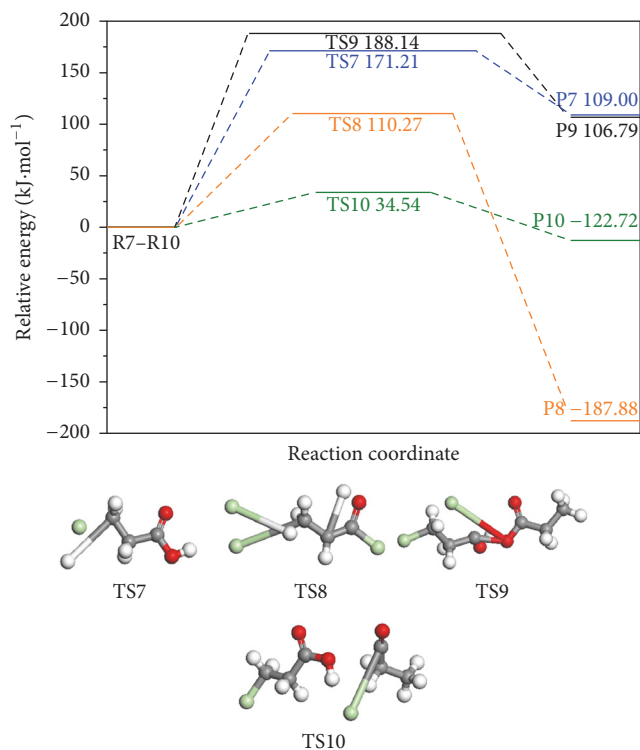
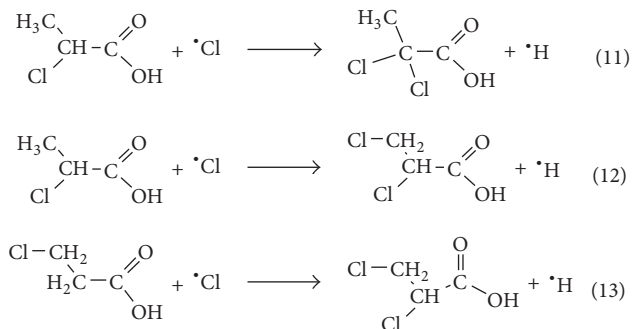


FIGURE 3: Potential energy diagram of the radical chlorination reactions related of byproducts together with the initial states, transition states, and final states.

formation route of β -chloropropanoic acid via ionic chlorination mechanism (Scheme 2; see (8)–(10)).

The formation of β -chloropropanoic acid via ionic chlorination mechanism is as follows. First, propanoyl chloride conducted enolization (Scheme 1; see (3)) and formed 1-propen-1-ol,1-chloro, and the corresponding primitive activation energy was 125.73 kJ/mol. Then, the double bond



SCHEME 3: The radical chlorination mechanism of byproducts.

in 1-propen-1-ol, 1-chloro was apt to react with chlorine (Scheme 2; see (8)) and formed β -chloropropanoyl chloride, and the corresponding primitive activation energy was 110.27 kJ/mol. Finally, the OH and Cl exchange reaction generated β -chloropropanoic acid (Scheme 2; see (9) and (10)) and its activation energy was 188.14 kJ/mol and 34.54 kJ/mol. Compared to these two kinds of paths which generated β -chloropropanoic acid and α -chloropropanoic acid, the activation energy of the formed β -chloropropanoic acid (Scheme 2; see (9)) was higher than that of the formed α -chloropropanoic acid (Scheme 1; see (6)). Therefore, it is difficult to form β -chloropropanoic acid by ionic chlorination.

3.4. Radical Chlorination Mechanism of Byproducts. The radical chlorination mechanism consists of successive chlorination steps. Initially, the α -chloropropanoic acid and β -chloropropanoic acid were formed and then further chlorinated to α,α -dichloropropanoic acid and α,β -dichloropropanoic acid (Scheme 3). The activation energies (E_a) and reaction energies (ΔH) calculation results are shown in Table 1. The energy potential diagram of the primitive reaction and the corresponding reactants, transition states, and products configuration is presented in Figure 4.

The activation energy of radical chlorination reaction which generated β -chloropropanoic acid (Scheme 2; see (7)) and α,α -dichloropropanoic acid (Scheme 3; see (11)) was 171.21 kJ/mol and 162.64 kJ/mol, respectively. They were lower than the activation energy of generated α,β -dichloropropanoic acid, which were 180.08 kJ/mol and 178.87 kJ/mol (Scheme 3; see (12)) and 187.87 kJ/mol (Scheme 3; see (13)). Therefore, β -chloropropanoic acid and α,α -dichloropropanoic acid are the main byproducts.

The activation energy of generated β -chloropropanoic acid (Scheme 2; see (7)) was 171.21 kJ/mol, higher than 125.73 kJ/mol (Scheme 1; see (3)), which was the rate-determining step of generating α -chloropropanoic acid. The amount of generated β -chloropropanoic acid changed with time which was different from α -chloropropanoic acid in this experiment. Thus, the generation of α -chloropropanoic acid was mainly through the acid-catalyzed enolization route, while β -chloropropanoic acid was mainly through the radical chlorination route.

Compared to these two kinds of paths which generated α,β -dichloropropanoic acid, the activation energy of

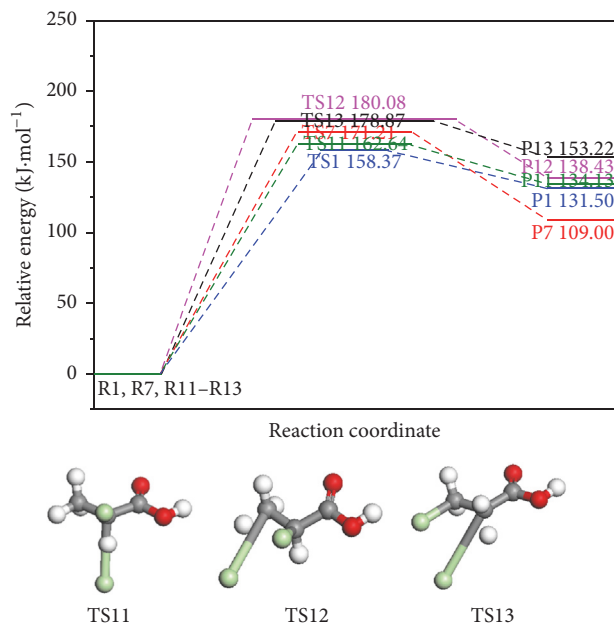
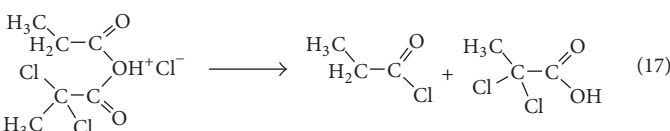
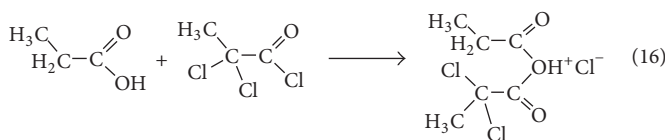
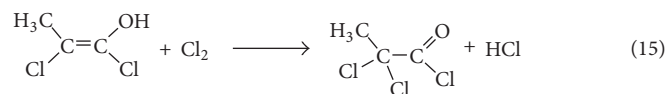
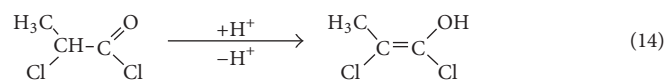
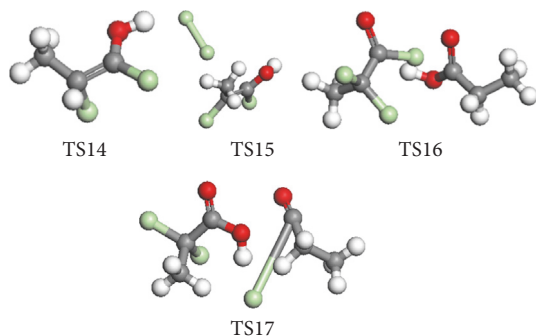
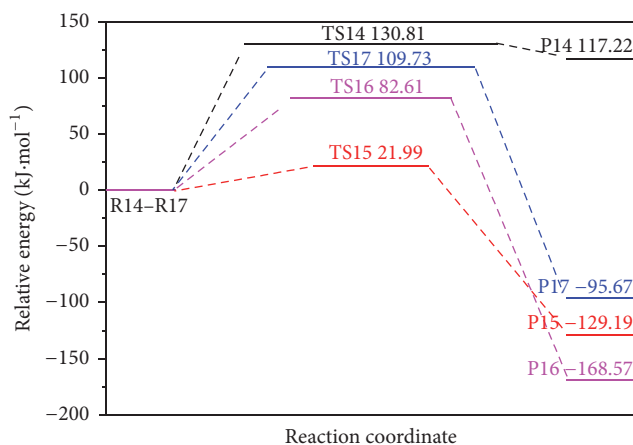


FIGURE 4: Potential energy diagram of the radical chlorination mechanism of byproducts together with the initial states, transition states, and final states.

the formed β -chloropropanoic acid (Scheme 2; see (7)) was higher than that of the formed α -chloropropanoic acid (Scheme 1; see (3)). Therefore, the formation of α,β -dichloropropanoic acid could be inhibited through inhibiting the formation of β -chloropropanoic. But the quantity of α,β -dichloropropanoic acid is hardly detected in the experiment.

3.5. Ionic Chlorination Mechanism of α,α -Dichloropropanoic Acid. In order to explore whether the formation between α,α -dichloropropanoic acid and α -chloropropanoic acid was a consecutive reaction, the paths in ionic chlorination mechanism were designed (Scheme 4). The path (Scheme 4; see (14)), the intermediate in the process generating α -chloropropanoyl chloride, can also generate 1-propenol, 1,2-dichloro. The consecutive chlorination of 1-propenol, 1,2-dichloro with chlorine generated α,α -dichlorine propanoyl chloride (Scheme 4; see (15)). α,α -Dichlorine propanoyl chloride with propanoic acid generated α,α -dichloropropanoic acid (Scheme 4; see (16) and (17)). The OH-Cl exchange reaction generated the final product. At the same time, energy potential diagram of the primitive reaction, the corresponding reactants, transition states, and products of configuration is shown in Figure 5.

It was observed that activation energy 130.81 kJ/mol (Scheme 4; see (14)) was higher than 109.73 kJ/mol (Scheme 4; see (15)) which was the rate-determining step in ionic chlorination mechanism. α,α -Dichloropropanoic acid and α -chloropropanoic acid were generated at the same time in the process of ionic chlorination mechanism. However, further comparison showed that radical chlorination activation energy 162.64 kJ/mol (Scheme 3; see (11)) was higher than 130.81 kJ/mol (Scheme 4; see (14)). This implies that radical

SCHEME 4: The ionic chlorination mechanism of α,α -dichloropropanoic acid.FIGURE 5: Potential energy diagram of ionic chlorination of α,α -dichloropropanoic acid together with the initial states, transition states, and final states.

chlorination was not easier to occur than ionic chlorination, which means that ionic chlorination was the main reaction path. Although higher temperature was the main cause of generation of byproducts [10], it was also observed that the generation of α,α -dichloropropanoic acid was less before concentrated sulfuric acid was added. This implies that the increase of H^+ does accelerate the acid-catalyzed path where

the product was α,α -dichloropropanoic acid. It proved that the generation path of α,α -dichloropropanoic acid was ionic chlorination mechanism which also was the cause of the phenomenon of the generation of byproducts. The α,α -dichloropropanoic acid increased rapidly under the reaction conditions with higher temperature or excessive chlorine in intermittent industrial manufacture.

4. Conclusions

Based on the investigation of the mechanism of chlorination from propanoic acid to α -chloropropanoic acid, the results could be summarized as follows:

- (1) The activation energy of the ionic mechanism for α -chloropropanoic acid formation was lower than that of the radical mechanism. The ionic mechanism involved four reaction routes and was initiated by the acid-catalyzed enolization of propanoyl chloride. Additionally, the activation energy of the rate-determining step was the process of 1-propanol,1-chloro formed 1-propen-1-ol,1-chloro.
- (2) The formation route of β -chloropropanoic acid was mainly through propanoic acid radical chlorination mechanism. α,β -Dichloropropanoic acid is formed via a consecutive radical chlorination mechanism.
- (3) The ionic mechanism of α,α -dichloropropanoic acid showed that the ionic chlorination was the main reaction path, and it was not easier for radical chlorination to occur compared with ionic chlorination for generation of α,α -dichloropropanoic acid. Hence, the formation route of α,α -dichloropropanoic acid and α -chloropropanoic acid was consecutive reaction. The formation of α,α -dichloropropanoic acid was mainly by α -chloropropanoic acid consecutive ionic chlorination mechanism which indicated that α -chloropropanoic acid is the key intermediate for α,α -dichloropropanoic acid formation process.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

All calculations in this paper were accomplished in the Key Laboratory of Coal Science and Technology, Ministry of Education and Shanxi Province. The authors are indebted to Professor Wang Baojun and Professor Zhang Riguang.

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