



Promotive Effects in α -Monochloropropionic Acid Catalytic Synthesis with Propionic Anhydride

JIANWEI XUE*, BEIBEI QI, XIAOGUANG WEN, YINGYING WANG, ZHIPING LV and FUXIANG LI

Research Institute of Special Chemicals, Taiyuan University of Technology, Taiyuan 030024, P.R. China

*Corresponding author: Tel/Fax: +86 351 6111178; E-mail: xuejianwei@yeah.net

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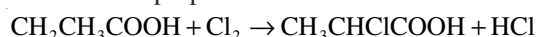
Selective α -chlorination of propionic acid to synthesize α -monochloropropionic acid was investigated in a laboratory-scale at 130 °C at atmospheric total pressure and in the presence of propionic anhydride as catalyst. Sulfuric acid and common Lewis acid were selected as promotive catalysts considering that the acid-catalyzed enolization is the rate determining step in the chlorination reaction of this experiment, also the reaction selectivity and activity were discussed in the presence of promotive catalysts. The studies revealed that the ferric chloride and sulfuric acid all have prominent promotive effects. Typically the amount of α -monochloropropionic acid can reach 96.14 % when 0.07 g of ferric chloride was added. Furthermore, our results demonstrated that the reaction selectivity and activity were dramatically enhanced after introducing Lewis acid as promotive catalysts.

Keywords: α -Monochloropropionic acid, Promotive effect, Lewis acid.

INTRODUCTION

α -Monochloropropionic acid (α -CPA) has an active chemical property and is used as a reaction intermediate in the chemical industry. It is widely used in the field of fine chemistry engineering, such as producing pesticides, dyestuff, agriculture, forestry and pharmaceuticals^{1,2}. Especially, it has remarkable application in pesticide³, well used for the synthesis of α -alanine⁴, methyl 2-chloropropionate and ethyl-2-chloropropionate^{5,6}. It is noted that this kind of bactericide and herbicide made of α -monochloropropionic acid not only has a significant efficacy, but also has little toxic effect. Naturally, the quantity of α -monochloropropionic acid demanded is increasing year by year.

The use of α -monochloropropionic acid is based on the reactivity of the α -carbon, which carries a partial positive charge and thus can react readily in nucleophilic substitution. In this paper, α -monochloropropionic acid was synthesized via chlorination of propanoic acid²:



The chlorination was carried out in the presence of propionic anhydride^{7,8} catalyst. However, to obtain a high catalytic effect, it is necessary to add a promotive catalyst to the reaction mixture. Considering that the acid-catalyzed enolization is the rate determining step in the chlorination reaction, we use Lewis acid as promotive catalysts to enhance the activity of the catalyst, accelerate the reaction rate, shorten the reaction cycle and thus increase the α -monochloropropionic acid yield. We explore

the effects of several kinds of Lewis acids acting as promotive catalysts on the reaction selectivity and activity. Also, the underlying reaction mechanisms were well discussed.

EXPERIMENTAL

Propionic acid (> 99 %, Alfa Aesar 79094), propionic anhydride (> 97 %, Alfa Aesar 123626), α -Monochloropropionic acid (> 97 %, Alfa Aesar 598787), ethyl acetate (> 99.5 %, Alfa Aesar 141786), FeCl_3 (> 98 %, Alfa Aesar 7705080), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (> 98 %, Alfa Aesar 10025771), ethanol anhydrous (> 85.8 %, Alfa Aesar 64175), anhydrous calcium chloride, chlorine, ammonia were all analytical pure; 98 % concentrated sulfuric acid was industrial product; FeCl_3/C was made by ourselves. DLSB-5/40 low-temperature pump; HJ-3 digital thermostat magnetic stirrer; TG328 analytical balance; 101-2 drying oven; GC-900 gas chromatograph.

Synthesis of α -monochloropropionic acid: A certain amount of propionic acid and propionic anhydride was added to a home-made glass reaction tube and the circulation solution (the molar ratio between ethylene glycol and water was 1:1) was added to the low-temperature pump. Then, the oil bath was stirred. After the oil heated to the desired reaction temperature and the coolant liquid temperature was cooled to -30 °C, the chlorine feed was introduced and the time began to be started with the flow rate of the chlorine was constant during the progress of the reaction. Samples of the chlorinated liquid for analysis were withdrawn at regular times and in a fixed quantity until the reaction finished. The exhaust gas was

emptied after passing through the water, sodium bicarbonate solution and concentrated sodium hydroxide solution.

The samples were gas chromatography analyzed as esters using ethanol as esterification agent for the samples were corrosive solutions. Then, the reaction yield was obtained by computation.

Preparation of promotive catalyst FeCl₃/C: A solution of FeCl₃·6H₂O (100 g) and activated carbon powder (50 g) in ethanol (25 mL) was refluxed for 0.5 h at 80 °C. After completion of the reaction, the product was filtrated and successively washed with ethanol until the product became colourless. Then, the product was filtered and activated in an oven for 2 h at 120 °C, the product was taken in the dryer in the end of the experiment⁹⁻¹².

Gas-chromatography analysis: In this paper, the corrected area normalization method was used for the quantitative analysis, the formula is as following:

$$W_i \% = \frac{F_{wi} \times A_i \times 100}{\sum F_{wi} \times A_i}$$

In the formula: W_i % = the quality ratio of i component acid; F_{wi} = the quality correction factor of i component acid; A_i = the chromatographic peak area of i component acid.

Infrared spectroscopic analysis: Potassium bromide semi-quantitative table method was used for infrared spectroscopic analysis. Due to the strong corrosion of α -monochloropropionic acid, so the best way to determine α -monochloropropionic acid is to get it spreaded on KBr.

The group peak positions of sample (a) and α -chloropropionic acid (b) are identical. The stretching vibration peak of C-Cl bond is observed at 700 cm⁻¹. Another stretching vibration peak at 1750 cm⁻¹ is assigned to be acid monomer of C=O. Two absorption peaks at 1440 and 920 cm⁻¹, which are relatively strong and wide, are bending vibration absorption peak due to the -OH group of carboxylic acid. The stretching vibration peak of methyl is at 2960 cm⁻¹. The peak at 3000 cm⁻¹, which is wide and scattered, is the stretching vibration absorption peak of O-H. Therefore, it was considered that the main product was α -monochloropropionic acid. It implies that the product synthesized by chlorination is relatively high without any impurity peak.

RESULTS AND DISCUSSION

Effect of different types of Lewis acid promotive catalysts on the chlorination of propionic acid: The effect of different types of Lewis acid was investigated were performed at 130 °C using a propionic acid addition of 14.9 g. The propi-

onic anhydride was added 20 mol % of the propionic acid and the promotive catalyst was added 0.1 g. In the presence of a slight excess of chlorine, the effects of different types of Lewis acid promotive catalysts and no promotive catalyst on the chlorination of propionic acid were studied respectively.

The experimental results obtained with different promotive effects on promotive catalytic activity selectivity with reaction are depicted in Table-1. The experiments revealed that when 98 % H₂SO₄, FeCl₃, FeCl₃·6H₂O, FeCl₃/C and SbCl₃ were added in the chlorination reaction solution, the content of main product α -monochloropropionic acid all increased. The results showed that the 98 % H₂SO₄ got the best promotive effect, the FeCl₃ was second and the FeCl₃·6H₂O, FeCl₃/C, SbCl₃ also demonstrate certain promotive effect. In the presence of 0.1 g 98 % H₂SO₄, the content of α -monochloropropionic acid reached 91.08 % after 2.5 h. However, the activated carbon got poor promotive catalytic activity and weak selectivity.

The experimental results obtained with different acids effects on promotive catalytic activity selectivity are depicted in Fig. 1. The results from our investigations are summarized that a higher reaction rate was obtained with the addition of 98 % H₂SO₄, because the chlorination reaction is an acid-catalyzed reaction. The reaction system got a raised acidity, the reaction direction toward the positive reaction and the reaction time was shortened at the same time. However, as a porous material the activated carbon had no promotive catalytic activity in the reaction system. This can be explained that the acid-catalyzed enolization is the rate determining step in the chlorination reaction and the activated carbon has no acidity. Meanwhile, the byproduct α,α -dichloropropionic acid increased due to chlorine adsorbed on the surface or pore structure of activated carbon and caused deep chlorination. In the presence of crystal water, FeCl₃·6H₂O would cause the main catalyst propionic anhydride part decomposed, which is equivalent to reducing the amount of the catalyst. Thereby, the catalysis effect was lower than that of FeCl₃. The catalysis activity of SbCl₃ was also lower than FeCl₃, because Sb³⁺ has a larger atomic radius than Fe atom and the ability of Sb³⁺ combining with propionyl chloride is lower than Fe³⁺. SbCl₃ is disadvantageous to the improvement of the competitiveness of the product for the high cost. So the promotive effect focused on 98 % H₂SO₄ and FeCl₃.

Influence of 98 % H₂SO₄ on chlorination: The chlorination reactions were carried out at 130 °C, the addition of propionic acid was 14.9 g, the propionic anhydride was added 20 mol % of the propionic acid and the chlorine feed was 40 mL/min. In the presence of a slight excess of chlorine, the

TABLE-1
COMPARISON OF DIFFERENT PROMOTIVE EFFECTS ON PROMOTIVE ACTIVITY SELECTIVITY WITH REACTION 2.5 h

Catalyst	Reaction time (h)	CA (%)	α -Monochloropropionic acid (%)	α,α -Dichloropropionic acid (%)	β -Monochloropropionic acid (%)
Blank	2.5	8.12	87.29	1.82	2.77
98 % H ₂ SO ₄ (0.1 g)	2.5	5.05	91.08	2.01	1.76
FeCl ₃ (0.1 g)	2.5	4.26	90.64	2.19	2.91
FeCl ₃ ·6H ₂ O (0.1 g)	2.5	1.76	89.71	4.64	3.89
FeCl ₃ /C (0.1 g)	2.5	6.42	88.68	2.38	2.52
SbCl ₃ (0.1 g)	2.5	2.23	88.02	5.13	4.52
Activated carbon (0.1 g)	2.5	17.28	68.23	10.47	4.02

Note: The above percentage is the percentage of quality

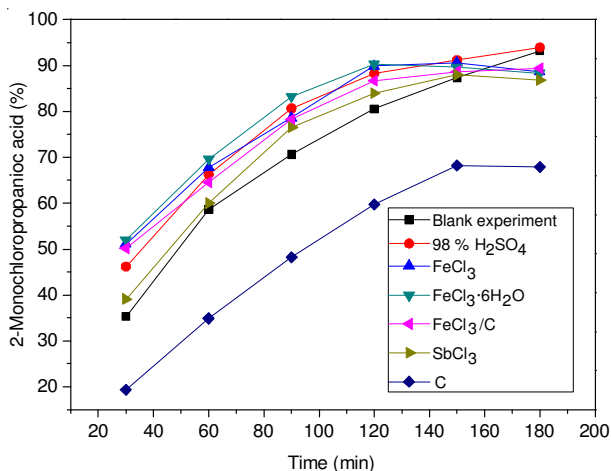


Fig. 1. Comparison of different acids effects on promotive catalytic activity selectivity

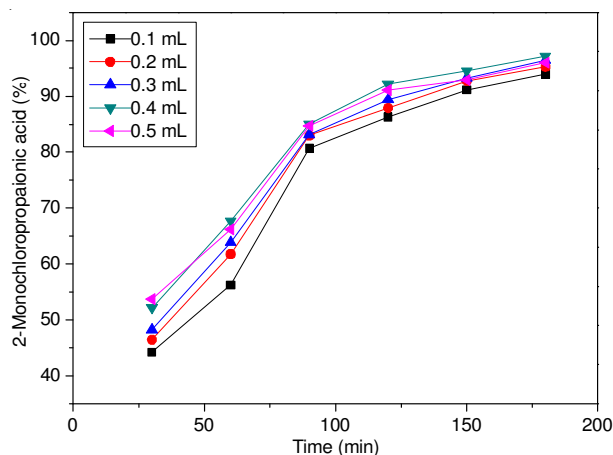
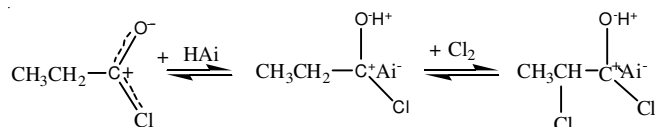


Fig. 2. Influence of different adding quantity of sulfuric acid on chlorination

influences of different adding quantity of 98 % H₂SO₄ were studied respectively.

The experimental results obtained with different adding quantity of sulfuric acid on chlorination are depicted in Table-2. The experiments revealed that the content of α -monochloropropionic acid gradually increased as the amount of 98 % H₂SO₄ increased from 0.1 mL to 0.5 mL and α -monochloropropionic acid content reached 97.22 % when the amount of 98 % H₂SO₄ was increased 0.4 mL. Whereas no higher yield was obtained with an increased addition, which may be explained that propionyl chloride and 98 % H₂SO₄ just reached complete reaction when the addition of 98 % H₂SO₄ was 0.4 mL. As the hydrogen proton quantity offered by 98 % H₂SO₄ exceeded the content of propionyl chloride, a certain influence on the reaction caused the content of α -monochloropropionic acid decreased.

The experimental results obtained with different adding quantity of 98 % H₂SO₄ are shown in Figs. 2-4. The experiments revealed that the selectivity of α -monochloropropionic acid showed a slow gradually trend. This can be explained that H₂SO₄ is a traditional proton acid catalyst, the combination of hydrogen with propionyl chloride according to the following mechanism:



98 % H₂SO₄ is proton acid and can easily combine with propionyl chloride in the chlorination reaction solution, so the enolization of propionyl chloride increased in the system and acted as promotive catalyst. Each hydrogen ion can only combine with one propionyl chloride molecule, so the promotive

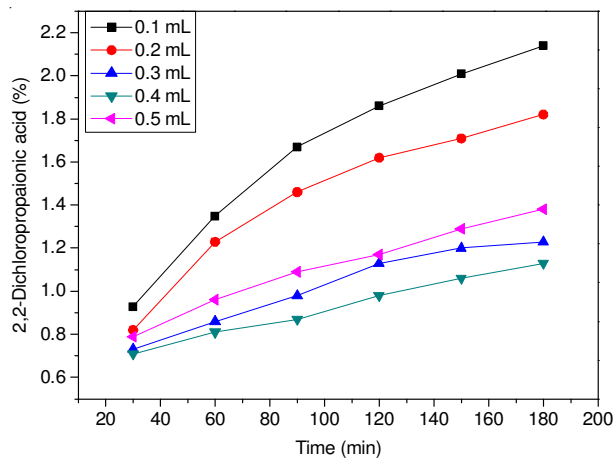


Fig. 3. Influence of different adding quantity of sulfuric acid on α,α -dichloropropionic acid

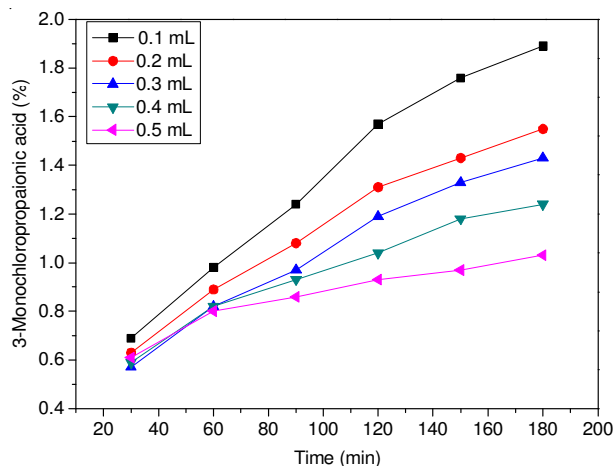


Fig. 4. Influence of different adding quantity of sulfuric acid on β -chloropropionic acid

TABLE-2
INFLUENCE OF DIFFERENT ADDING QUANTITY OF SULFURIC ACID ON CHLORINATION

H ₂ SO ₄ (mL)	Reaction time (h)	CA (%)	α -Monochloropropionic acid (%)	α,α -Dichloropropionic acid (%)	β -Monochloropropionic acid (%)
0.1	3	1.96	94.01	2.14	1.89
0.2	3	1.87	95.26	1.05	1.82
0.3	3	0.63	96.42	1.23	1.72
0.4	3	0.43	97.22	1.13	1.22
0.5	3	0.57	97.05	1.09	1.29

Note: The above percentage is the percentage of quality.

effect should be weaker than FeCl_3 . However, the concentration of hydrogen ion in one unit reaction solution in the presence of 98 % H_2SO_4 was higher than the content of Fe^{3+} after FeCl_3 added. The substances generated by hydrogen ions and propionyl chloride, whose molecular weight is smaller than the substances generated by Fe^{3+} and propionyl chloride, have a low boiling point and possibly escape from the reaction system. 98 % H_2SO_4 also has other shortcomings such as organic reactant dehydration, carbonization and caused the product colour deepened. In a summary, FeCl_3 shows a higher promotive catalytic activity.

Influence of different adding quantity of FeCl_3 on chlorination: The chlorination reactions were carried out at 130 °C, the addition of propionic acid was 14.9 g, the propionic anhydride was added 20 mol % of the propionic acid and the chlorine feed was 40 mL/min. In the presence of a slight excess of chlorine, the influences of different adding quantity of FeCl_3 were studied, respectively.

Fig. 5 revealed that different amount of FeCl_3 was added in the chlorination reaction solution, the content of main product α -monochloropropionic acid all increased greatly relative to the condition of no promotive added. When the reaction proceeded about 2.5 h, in the presence of 0.4 g FeCl_3 , the content of α -monochloropropionic acid reached 96.14 % which was far exceeded the 87.29 % of no promotive. Thus it can be seen that FeCl_3 has a better promotive effect and selectivity. The key step of propionic acid anhydride catalytic chlorination reaction is enolization transformation which is also acid-catalyzed process, so the overall reaction mechanism can be presented as follows:

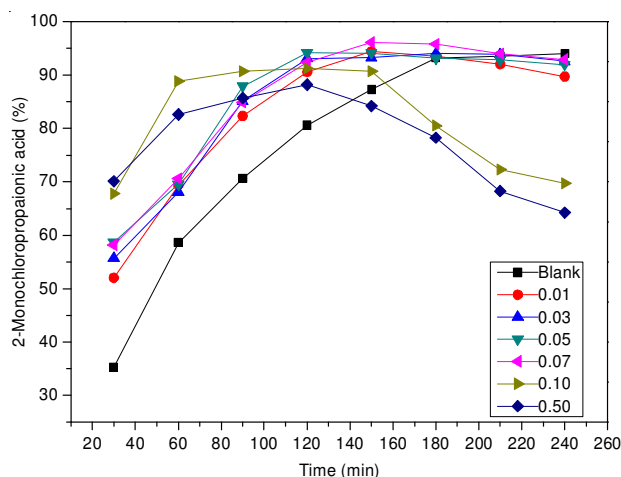
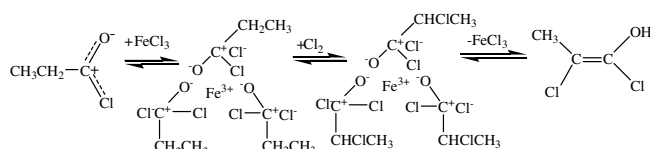
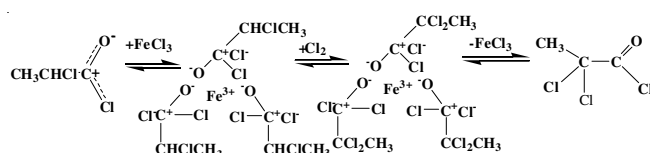


Fig. 5. Influence of different adding quantity of ferric chloride on 2-monochloropropionic acid content



In the reaction system, there was a large amount of propionyl chloride, Fe^{3+} is easy to make propionyl chloride enolization and generate complex. The oxygen atoms of propionyl chloride show electronegativity and combine with the three Lewis acid position of Fe^{3+} to form a large molecular structure, which reduces the activation energy of the reaction of propionyl chloride enolization. These complexes have a high boiling point and possibly escape from the reaction system, which increases the content of propionyl chloride enolization in the reaction solution. The enolization is the rate determining step of chlorination reaction. In a summary, FeCl_3 shows a higher promotive catalytic activity.

The experimental results obtained with different adding quantity of ferric chloride on 2-monochloropropionic acid content are depicted in Table-3. The content of α -monochloropropionic acid gradually increased as the amount of FeCl_3 increased, the promotive effect was the best when the amount was 0.07 g. Whereas the promotive effect decreased significantly when the amount of FeCl_3 exceeded 0.07 g and appeared depth chlorinated reaction. This may be explained that the reaction between α -monochloropropionic acid and α,α -dichloropropionic acid is a parallel reaction. The excessive FeCl_3 combines with the chlorinated enolization intermediates, which is conducive to the generation of α,α -dichloropropionic acid. Based on the above information, the mechanism can be represented as follows:



Influence of different adding quantity of FeCl_3/C on chlorination: The chlorination reactions were carried out at 130 °C, the addition of propionic acid was 14.9 g, the propionic anhydride was added 20 mol % of the propionic acid and the chlorine feed was 40 mL/min. In the presence of a slight excess of chlorine, the influences of different adding quantity of FeCl_3/C were studied respectively.

The experimental results obtained with different adding quantity of ferric chloride on chlorination are depicted in Table-4.

TABLE-3
INFLUENCE OF DIFFERENT ADDING QUANTITY OF FERRIC CHLORIDE ON CHLORINATION

Adding quantity of ferric chloride (g)	Reaction time (h)	CA (%)	α -Monochloropropionic acid (%)	α,α -Dichloropropionic acid (%)	β -Monochloropropionic acid (%)
0	2.5	8.12	87.29	1.82	2.77
0.01	2.5	1.66	94.44	2.18	1.72
0.03	2.5	1.12	93.62	3.12	2.14
0.05	2.5	0.67	94.13	2.83	2.37
0.07	2.5	0.24	96.14	1.83	1.79
0.10	2.5	4.26	90.64	2.19	2.91
0.50	2.5	5.12	84.19	7.40	3.29

Note: The above percentage is the percentage of quality.

TABLE-5
INFLUENCE OF DIFFERENT ADDING QUANTITY OF FERRIC CHLORIDE ON CHLORINATION

Adding quantity of ferric chloride/carbon (g)	Reaction time (h)	CA (%)	α -Monochloropropionic acid (%)	α,α -Dichloropropionic acid (%)	β -Monochloropropionic acid (%)
0	2.5	8.12	87.29	1.82	2.77
0.1	2.5	6.42	88.68	2.38	2.52
0.2	2.5	5.55	88.47	2.69	3.29
0.3	2.5	3.56	89.59	3.17	3.68
0.4	2.5	2.51	87.79	5.26	4.44
0.5	2.5	2.50	85.92	7.23	4.35

Note: The above percentage is the percentage of quality.

The experiments revealed that during 2.5 h reaction time the reaction rate and α -monochloropropionic acid gradually increased clearly with the addition of FeCl_3/C . Whereas the content of α,α -dichloropropionic acid also increased clearly as FeCl_3/C increased. This may be explained that FeCl_3 can promote the enolization of propionyl chloride and increase the content of propionyl chloride, this promotion still exists when part of the FeCl_3 loaded in the activated carbon. Chlorine can be adsorbed by the pore structure and the surface of activated carbon, which may provide favourable conditions for the dichloro reaction.

Conclusion

Based on our experimental results and previous observations, we have the conclusion that Lewis acid as promotive catalysts plays an important role in the acid catalysis process with propionic anhydride as catalyst. Lewis acid has a good promotive catalytic activity, which makes α -monochloropropionic acid content greatly increased, the reaction time effectively shortened, the reaction selectivity improved and the colour of the product was not influenced.

The results indicated that ferric chloride and sulfuric acid have good promotive catalytic effect. As protonic acid, 98 % H_2SO_4 provides larger amounts of H^+ and speeds up the reaction process. However, in consideration of the strong corrosive of 98 % H_2SO_4 and the strict requirements to the technological conditions, ferric chloride considered the best Lewis acid promotive catalyst due to its Lewis acid position can combines with propionyl chloride and generates a large amounts of

complex which effectively reduced the escape of propionyl chloride in the reaction progress. When the adding quality of ferric chloride was 0.07 g, the amount of α -monochloropropionic acid can reach 96.14 %, which effectively increase the reaction selectivity and reduce the cost of production.

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