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Microwave Synthesis of Chloroacetic Acid with Various Cocatalysts in Acetic Anhydride Catalyzing Method

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In this paper, we introduce a method of synthesizing chloroacetic acid using acetyl chloride as catalyst and anhydrous ferric chloride, ferric chloride hexahydrate, zinc chloride and concentrated sulfuric acid (98 % H_2SO_4) as cocatalysts respectively with a variable frequency microwave oven as heater. From investigating the influences of cocatalysts in reaction, we draw a optimal condition that the yield and selectivity of chloroacetic acid are 98.11 and 98.58 % respectively when adding 0.4 g $FeCl_3$ in mixture after reacting 3.5 h and in comparable with the corresponding percentages, 96.9 and 96.87 %, with 0.7 g $ZnCl_2$ adding, the adding amount of 1.5 g 98 % H_2SO_4 result in a little lower percentages of 95.71 and 95.61 % correspondingly. We have speculated the cocatalytic mechanisms in chlorination.

Keywords: Variable frequency, Microwave, Acetic Anhydride, Chloroacetic Acid, Cocatalyst.

INTRODUCTION

Chloroacetic acid is one of the most important raw and intermediate materials in organic synthesis and is widely used in medicine, pesticide, spice, dyestuff and so on. China as a huge nation of production and exporting in chloroacetic acid, keeping improving the production of chloroacetic acid on industrial production has a great meaning. Hence, the research and development in new productive technology and catalytic systems are the primary problems needed to be solved urgently.

A dozen or more synthesis methods of chloroacetic acid have been reported up to now and the process using acetic anhydride as catalyst is the most common one at home and abroad. But the cocatalyst also plays an important role in the chloroacetic acid synthesis process. The cocatalysts are usually divided into two categories[1]: one is Lewis acid, generally made up of some molecules or ions owning unoccupied orbitals which could accept lone pair, such as $FeCl_3$, $ZnCl_2$, BF_3 and so on; one is Bronsted acid, generally made up of H_2SO_4, HCl, CH_3COOH and so on.

Chloroacetic acid was first successfully synthesized using acetic anhydride as catalyst and concentrated sulfuric acid as cocatelyst by Martikainen *et al.*[2] in 1987. They revealed that the enolization of acetyl chloride was the control step of reaction rate in chlorination and he also found that the using of concentrated sulfuric acid in process could intensely accelerate the reaction rate. In 1988, a kinetic mathematic model for the chlorination reaction catalyzed by acetyl chloride as catalyst and concentrated H_2SO_4 as cocatalyst was reported founded by Salmi *et al.*[3]. Wang and Zhai[4] came up with a new theory that cocatalysts could effectively enhance the reaction reactivity and selectivity, which could be revealed by investigation of the activation energy in both main and deputy acetic acid chlorination reactions catalyzed by sulphur and by study of the chemical engineering kinetics and thermodynamics. Xu *et al.*[5] achieved the conditions on chlorination reaction influenced by H_2SO_4 which used as cocatalyst and acetic anhydride as catalyst.

We have performed an experiment[6] on synthesizing chloroacetic acid by chlorination of glacial acetic acid catalyzed by acetic anhydride in the environment of microwave but without any cocatalyst. In that part of experiment, the adding amount of acetic anhydride was approximately 20 % of glacial acetic acid in volume fraction with slightly excessive chlorine and we kept the rate of microwave in 300 W and adjusted the temperature of water bath in 70 °C in order to maintain the reaction temperature in 95 °C. After 3.5 h reaction, the production of chloroacetic acid reached to maximum of 94.31 % and the reaction selectivity of 93.01 %. On the basis of the previous experiment, we now discuss the influence of various cocatalysts on the chlorination reaction in the same synthesis system. By using different kinds of cocatalysts in synthesis process, such as Lewis acid ($FeCl_3$, $FeCl_3{\cdot}6H_2O$, $ZnCl_2$) and Bronsted acid (concentrated H_2SO_4), influences on cocatalytic activity and selectivity in chlorination reaction in microwave system is first discussed in this paper.

EXPERIMENTAL

Main reaction:

$$CH_3COOH + Cl_2 \xrightarrow[FeCl_3\,/\,FeCl_3\cdot 6H_2O\,/\,ZnCl_2\,/\,H_2SO_4]{CH_3COOCOCH_3} ClCH_2COOH + HCl$$

By reaction:

$$ClCH_2COOH + Cl_2 \xrightarrow[FeCl_3\,/\,FeCl_3\cdot 6H_2O\,/\,ZnCl_2\,/\,H_2SO_4]{CH_3COOCOCH_3} Cl_2CHCOOH + HCl$$

$$Cl_2CHCOOH + Cl_2 \xrightarrow[FeCl_3\,/\,FeCl_3\cdot H_2O\,/\,ZnCl_2\,/\,H_2SO_4]{CH_3COOCOCH_3} Cl_3CCOOH + HCl$$

The detailed reaction mechanism can be found in references[7-8].

Glacial acetic acid (> 99 %), acetic anhydride (≥ 99 %), absolute ethanol (≥ 99.8 %), anhydrous calcium chloride (≥ 94 %), ammonia solution (28 %), trichloromethane (≥ 99.95 %), ethylene glycol (A.R), all are purchased from TianYi Reagent Factory in Tianjin. Ferric chloride anhydrous ($FeCl_3$, ≥ 96 %) and ferric chloride hexahydrate ($FeCl_3\cdot 6H_2O$, ≥ 97 %) are from LaiZhou HaiXin Chemical Co., Ltd. And sodium hydroxide (≥ 96 %) and zinc chloride (≥ 96 %) are from Northern Sky Reagent Factory in TianJin. Concentrated sulfuric acid (98 %) is from Chemical Insecticide Factory in Taiyuan.

Infrared thermometer (UT300A), YaChen Electronic Technology Company in Shenzhen; gas chromatograph (GC-900), HaiXin Chromatographic Instrument Company in Shanghai; the variable frequency microwave reactor (EV923KF6-NA), Midea Microwave Electric Appliance Company in Guangdong.

Chlorination reaction: After adding 50 mL glacial acetic acid, 10 mL acetic anhydride and different amounts of cocatalysts ($FeCl_3$, $FeCl_3\cdot 6H_2O$, $ZnCl_2$ and concentrated H_2SO_4) respectively to the reaction vessel, keeping the rate of microwave in 300 W and reaction temperature in 95 °C, the catalytic activity and selectivity of chloroacetic acid are studied in the condition of slightly excessive chlorine.

Esterification reaction: Adding 2 mL CH_3CH_2OH, 1 mL concentrated H_2SO_4 and 1 mL hydrochloric from the chlorination reaction to a dry test tube with ground plug, tightly closed, packed with tape, then immediately putting it in boiling water for 5 min. Then cooling down with running water, adding 6 mL distilled water and 1.5 mL trichloromethane, intensely shaking the tube for a while, stratification for a moment and then absorbing a certain amount of oil in sublayer to a tiny bottle with a couple of calcium chloride anhydrous preparing for gas chromatography.

RESULTS AND DISCUSSION

Influence of cocatalyst ferric chloride on chlorination reaction: Fig. 1 shows the changes of the production of chloroacetic acid as increases of reaction time in the range of 0-3.5 h with different amount of $FeCl_3$ in synthesis system. It is obvious that almost the curves except 0.2 and 0.3 g are all above the curve of blank (Fig. 1), which means that a certain amount of cocatalyst $FeCl_3$ is especially favorable for cocatalyzing of the chlorination. When reacting for 3 h, the curves begin to flatten and then reach to maximum at 3.5 h and it is apparently that the yield of chloroacetic acid has a tendency to increase over the amount of $FeCl_3$. This phenomenon may result from the two kinds of cocatalyzation caused by $FeCl_3$: one, normally, enhanced enolization of acetyl chloride; the other one, formation of macromolecular complex (**Scheme-I**). Lewis acid centers are formed when $FeCl_3$ is dissolved in synthesis mixture; and because of the complextion of Lewis acid centers and nucleophilic site, the activation energy of regent has been decreased and the content of acetyl chloride could be increased in the mixture, promoting the catalyzation of chlorination.

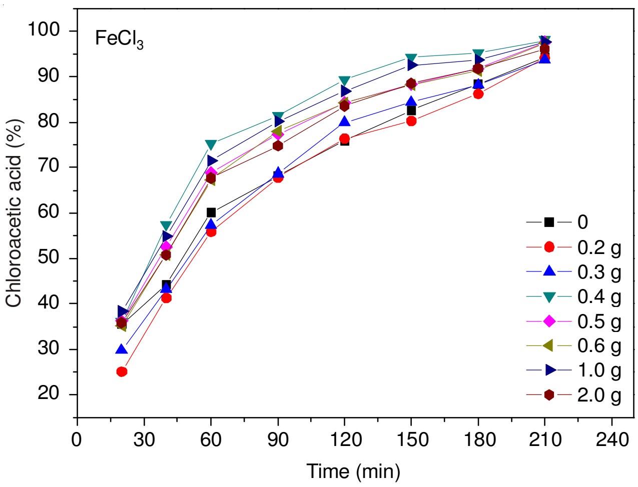
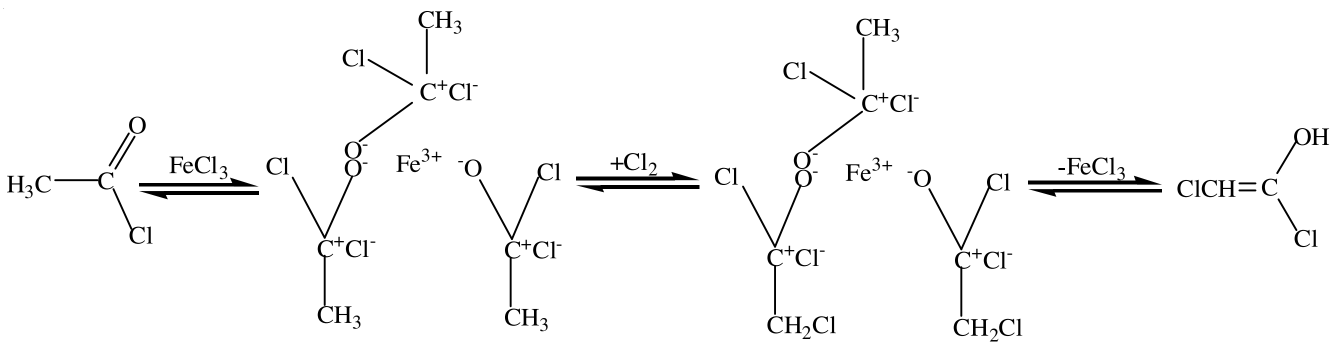


Fig. 1. Influence of cocatalyst FeCl3 on the production of chloroacetic acid. The different amounts of $FeCl_3$ added in mixture are 0, 0.2, 0.3, 0.4, 0.5, 0.6, 1 and 2 g, respectively

The detailed cocatalytic mechanism of ferric chloride has been shown in **Scheme-I**. It is known that the acetyl chloride could easily escape to the upper gas phase in the system of microwave heating, so the macromolecular complex formed in **Scheme-I** can effectively retain the acetyl chloride in liquid phase and fasten the reaction rate.



Scheme-I: Cocatalytic mechanism of $FeCl_3$ on chlorination reaction

As shown in Table-1, after reacting for 3.5 h, the production of chloroacetic acid increases slowly as $FeCl_3$ growth until to 0.4 g and the content of chloroacetic acid in reaction mixture reach to the maximum of 98.11 % and the corresponding reaction selectivity is 98.58 %. Then the percentage of chloroacetic acid in mixture and selectivity show a slightly decrease as the continuous growth in $FeCl_3$, on the contrary, the percentage of dichloroacetic acid shows a growth trend. Eventually, we choose 0.4 g $FeCl_3$ as the optimum additional quantity.

TABLE-1
INFLUENCE OF DIFFERENT ADDING AMOUNT OF COCATALYST $FeCl_3$ ON CHLORINATION

Adding amount of $FeCl_3$ (g)	Reaction time (h)	ACA (%)	MCA (%)	DCA (%)	Selectivity (%)
0	3.5	3.47	94.31	2.22	93.01
0.2	3.5	4.17	94..22	1.61	92.40
0.3	3.5	4.56	93.78	1.66	91.78
0.4	3.5	0.03	98.11	1.86	98.58
0.5	3.5	0.35	97.61	2.04	97.95
0.6	3.5	0.40	97.47	2.13	97.80
1	3.5	0.39	97.66	1.96	97.95
2	3.5	0.42	96.21	3.37	96.85

Influence of the crystal water in ferric chloride hexahydrate on chlorination reaction: Keeping a constant mol of Fe^{3+} with 0.4 g $FeCl_3$, we add 0.67 g $FeCl_3·6H_2O$ in synthesis mixture.

Some interesting points have found in Fig. 2 that the production of chloroacetic acid cocatalyzed by $FeCl_3$ is higher than that by $FeCl_3·6H_2O$ at the early stage of the reaction, may be resulted from the consumption of catalyst acetyl chloride by crystal water in $FeCl_3·6H_2O$ and the cocatalytic activity exhibit a similar tendency in later stage reaction, likely caused by the full dissolution of $FeCl_3$ which provide almost same amount of Fe^{3+} as cocatalytic center.

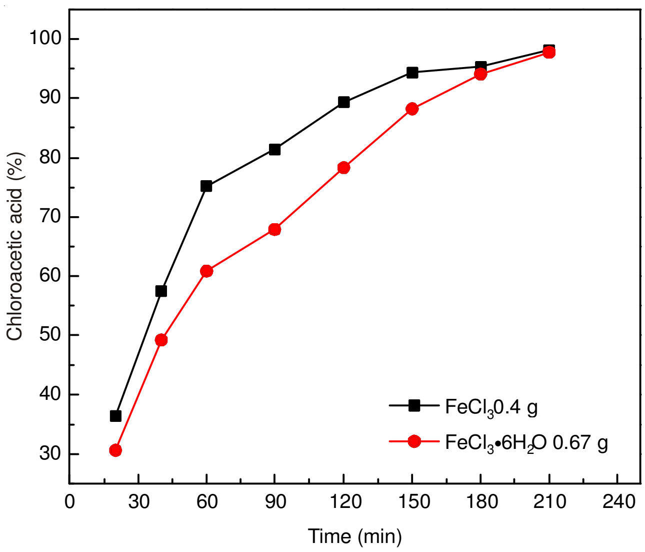


Fig. 2. Influence of the crystal water in $FeCl_3·6H_2O$ on the production of chloroacetic acid

As shown in Table-2, after reacting for 3.5 h, the yield of chloroacetic acid with $FeCl_3$ and $FeCl_3·6H_2O$ as cocatalyst are 98.11 and 97.79 % respectively and the reaction selectivity

TABLE-2
INFLUENCE OF CRYSTAL WATER IN $FeCL_3·6H_2O$ ON CHLORINATION

Cocatalysts	Adding quantity (g)	Reaction time (h)	ACA (%)	MCA (%)	DCA (%)	Selectivity (%)
$FeCl_3$	0.4	3.5	0.03	98.11	1.86	98.58
$FeCl_3·6H_2O$	0.67	3.5	0.17	97.79	2.04	98.23

are 98.58 and 98.23 %, which all present an almost identical result whether in cocatalytic activity or selectivity. So we draw the conclusion that crystal water in $FeCl_3·6H_2O$ almost make no difference with $FeCl_3$ after reacting for 3.5 h.

Influence of cocatalyst zinc chloride on chlorination reaction: The production of chloroacetic acid increases with time and displays a tendency of increasing at the beginning and then decreasing with the content of $ZnCl_2$ in mixture as shown in Fig. 3. Almost all the curves except 1 g are over the curve of blank without $ZnCl_2$ adding, which indicating that the cocatalyst $ZnCl_2$ has a positive effect in terms of improving the chloroacetic acid production on chlorination reaction. This, like cocatalyst $FeCl_3$, may also caused by the improved enolization of acetyl chloride and the raised concentration of acetyl chloride in mixture as a result of the formation of a macromolecular complex in **Scheme-II** which illustrate the detailed $ZnCl_2$ cocatalytic mechanism. Zinc chloride has two Lewis acid centers and can attract two acetyl chloride molecules nearby, preserving the acetyl chloride from escaping to gas phase; and then the reaction rate and activity will be boosted significantly.

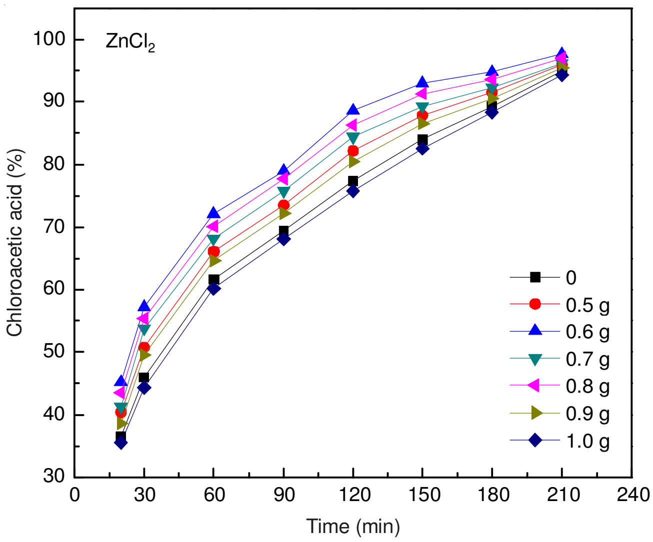
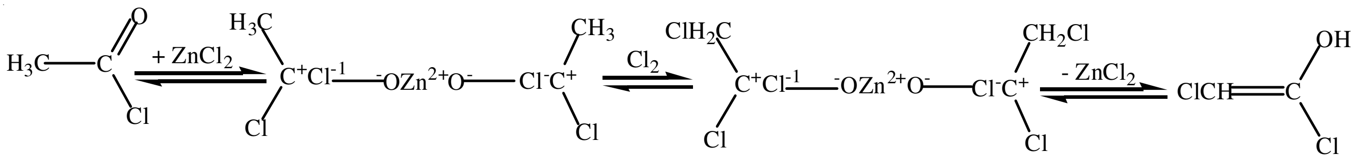


Fig. 3. Influence of cocatalyst $ZnCl_2$ on the production of chloroacetic acid. The different amounts of $ZnCl_2$ added in mixture are 0, 0.5, 0.6, 0.7, 0.8, 0.9 and 1 g, respectively

From Table-3, after reacting for 3.5 h, we can find that the yield of chloroacetic acid reach to the maximum of 97.71 % and the corresponding selectivity is 98.08 %, also the maximum, after adding 0.7g $ZnCl_2$; then the percentages of chloroacetic acid in mixture and selectivity all show a slightly decrease as the continuous growth in $ZnCl_2$. On the contrary, the percentage of dichloroacetic acid shows a tendency to grow. Finally, we choose 0.7 g $ZnCl_2$ as the optimum additional quantity.



Sheme-II: Cocatalytic mechanism of $ZnCl_2$ on chlorination reaction

TABLE-3
INFLUENCE OF DIFFERENT ADDING AMOUNT OF COCATALYST $ZnCl_2$ ON CHLORINATION

Adding quantity of $ZnCl_2$ (g)	Reaction time (h)	ACA (%)	MCA (%)	DCA (%)	Selectivity (%)
0	3.5	3.47	94.31	2.22	93.01
0.5	3.5	3.9	94.93	1.17	93.13
0.6	3.5	2.68	96.01	1.31	94.88
0.7	3.5	0.28	97.71	2.01	98.08
0.8	3.5	2.04	96.2	1.76	95.53
0.9	3.5	1.0	97.02	1.98	96.97
1.0	3.5	2.27	95.48	2.25	94.81

TABLE-4
INFLUENCE OF DIFFERENT ADDING AMOUNT OF COCATALYST 98 % H_2SO_4 ON CHLORINATION

Adding amount of 98 % H_2SO_4 (g)	Reaction Time (h)	ACA (%)	MCA (%)	DCA (%)	Selectivity (%)
0	3.5	3.47	94.31	2.22	93.01
0.5	3.5	2.98	94.68	2.34	93.66
1.0	3.5	2.19	95.14	2.67	94.62
1.5	3.5	1.48	95.71	2.81	95.61
2.0	3.5	2.10	94.98	2.92	94.57

ACA = Acetic acid; MCA = Monochloroacetic acid; DCA = Dichloroacetic acid

Influence of cocatalyst concentrated sulfuric acid (98 % H_2SO_4) on chlorination reaction: It is obviously in Fig. 4 that the curves have a trend that the percentages of chloroacetic acid in mixture increase firstly and then decrease slightly with the amount of H_2SO_4. All the curves are above the curve of blank, demonstrating the positive impact of cocatalyst H_2SO_4 on increasing the production of chloroacetic acid. The reservation of acetyl chloride in synthesis mixture is a critical step on chlorination before the content of chloroacetic acid can be improved. This phenomenon may be just attributed to the promoted enolization of acetyl chloride by H_2SO_4 as $FeCl_3$ and $ZnCl_2$ and without the formation of macromolecular complex. Table-4 shows that the mixture with 1.5 g addition of concentrated sulfuric acid owns the largest percentage of chloroacetic acid that reaches 95.71 % and also the largest reaction selectivity of 95.61 % in comparison with the rest of addictive amount after the reaction being carried out for 3.5 h. So we choose 1.5 g addictive amount of concentrated sulfuric acid as the optimum condition.

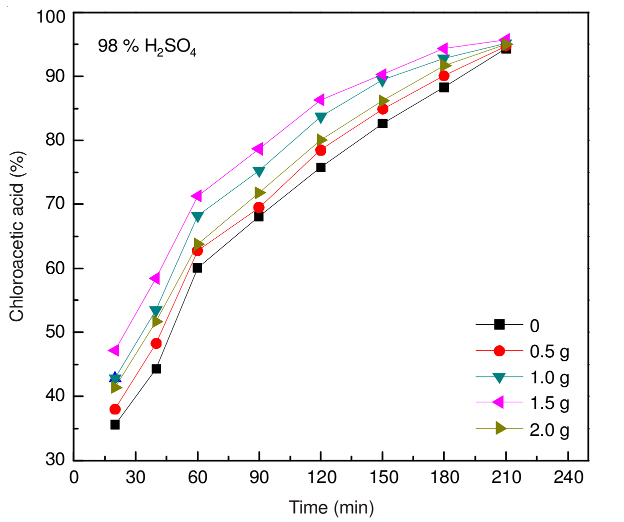


Fig. 4. Influence of cocatalyst 98 % H_2SO_4 on the production of chloroacetic acid. The different amounts of H_2SO_4 added in mixture are 0, 0.5, 1, 1.5 and 2 g, respectively

Conclusion

From investigating of the different cocatalysts on chlorination reaction in microwave environment, it is obvious that the catalytic activity and selectivity have been significantly promoted by using of whether Bronsted acid (H_2SO_4) or Lewis acid ($FeCl_3$, $ZnCl_2$). We find that the Lewis acid show slightly greater cocatalytic activity and selectivity than Bronsted acid, which may result from the reason that $FeCl_3$ and $ZnCl_2$ not merely accelerate the enolization of acetyl chloride but also raise its concentration in mixture through the formation of macromolecular complex and $FeCl_3$ is a better one in comparable with $ZnCl_2$. So we draw a conclusion that the optimum condition in synthesis of chloroacetic acid will be reached when the adding amount of cocatalyst $FeCl_3$ is 0.4 g in reaction mixture and 98.11 % production of chloroacetic acid and 98.58 % selectivity are all relatively highest after reacting for 3.5 h.

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