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Investigation of the kinetics and mechanism of the glycerol chlorination reaction using gas chromatography–mass spectrometry

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Abstract: As a primary by-product in biodiesel production, glycerol can be used to prepare an important fine chemical, epichlorohydrin, by the glycerol chlorination reaction. Although this process has been applied in industrial production, unfortunately, less attention has been paid to the analysis and separation of the compounds in the glycerol chlorination products. In this study, a convenient and accurate method to determine the products in glycerol chlorination reaction was established and based on the results the kinetic mechanism of the reaction was investigated. The structure of main products, including 1,3--dichloropropan-2-ol, 2,3-dichloropropan-1-ol, 3-chloro-1,2-propanediol, 2-chloro-1,3-propanediol and glycerol was ascertained by gas chromatography–mass spectrometry and the isomers of the products were distinguished. Apidic acid was considered as the best catalyst because of its excellent catalytic effect and high boiling point. The mechanism of the glycerol chlorination reaction was proposed and a new kinetic model was developed. Kinetic equations of the process in the experimental range were obtained by data fitting and the activation energies of each tandem reaction were 30.7, 41.8, 29.4 and 49.5 kJ mol^{-1}, respectively. This study revealed the process and mechanism of the kinetics and provides the theoretical basis for engineering problems.

Keywords: glycerol; monochloropropanediol; dichloropropanol; chlorination reaction; gas chromatography–mass spectrometry; kinetic model.

INTRODUCTION

Epichlorohydrin is an important fine chemical, which is widely used to prepare organic chemical raw materials such as epoxy resin.[1,2] In China, the production capacity of epichlorohydrin had reached 497 thousand tons until 2008

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and it is estimated that demand for it will have reached 700 thousand tons in 2012. Currently, the methods to produce epichlorohydrin include the high-temperature chlorination of propylene route and the allyl acetate route,[3,4] which depend on the petroleum industry. Then, with the petroleum energy crisis in recent years and the soar of oil prices, the price of epichlorohydrin on the international market rose. Due to the increase in the production of the biodiesel industry in recent years and the consequential increase in its by-product glycerol (one tenth of the yield of biodiesel), there is an oversupply of glycerol and a slump in its price on the market. The efficient and reasonable utilization of glycerol has become a bottleneck problem for the healthy development of the biodiesel industry chain. Dichloropropanol (DCP), as the raw material of epichlorohydrin production, can be produced by the reaction between glycerol and hydrogen chloride. Thus, the process of preparing epichlorohydrin from glycerol would allow mankind to be less dependent on petroleum and promote the development of the biomass energy industry, which has great economic and social values.

The most important step in the synthesis of DCP from glycerol is the chlorination reaction glycerol.[5,6] This process has been introduced on the industrial scale[7–9] but, unfortunately, less attention has been paid to the analysis and separation of the compounds produced in the reaction. Therefore, there is an urgent need for the development of an accurate method to determine the compositions in this complex reaction system. To date, the primary method for analyzing monochloropropanediol (MCP) and DCP is gas chromatography.[10] Schuhmacher *et al*. and Crews *et al.* determined 1,3-dichloropropan-2-ol (1,3-DCP) by gas chromatography–mass spectrometry (GC–MS).[11,12] Furthermore, Boden *et al*. and Chung *et al.* both reported methods for the simultaneous analysis of 3-chloro-1,2-propanediol (3-MCP) and 1,3-DCP by GC–MS.[13,14] However, the above-mentioned methods not only required the samples to be derivatized before analysis, but also they cannot recognize the isomers present in the reaction system. In addition, the formation of the intermediate MCP complicates the reaction system and causes great difficulties for further research on the dynamics of the reaction. In this study, a GC–MS method that can simultaneously ascertain the composition, including glycerol, 3-MCP, 2-chloro-1,3-propanediol (2-MCP), 1,3-DCP and 2,3-dichloropropan-2-ol (2,3-DCP), in the chlorination reaction system was developed without the necessity of derivatization, which effectively simplified the analysis process and enabled the isomers in products to be distinguished, thus providing a fast and convenient method for further study of the dynamics of the reaction.

Hitherto, there have been only a few reports concerning the kinetics of the glycerol chlorination reaction.[15] Siano *et al.* found that propionic acid was the best catalyst for this reaction, although its boiling point is only slightly higher than that of acetic acid, which is used in the traditional process. They considered that an oxonium group was formed during the glycerol chlorination process and

deduced a dynamic model of the chlorination tandem reactions.[16] However, there were some defects in their hypothesis and the model cannot completely accurately describe the glycerol chlorination process. In this study, the chlorination reaction model has been improved, which reflected the mechanism of the reaction and offered a theoretical basis for the industrial production of epichlorohydrin.

EXPERIMENTAL

Materials and instruments

All chemicals used in the present work, *viz*., glycerol, acetic acid, propanoic acid, malonic acid, succinic acid and apidic acid (all purchased from Ludu, China) were of analytical reagent (A.R.) grade.

Gas chromatographic and mass spectrometric analysis

The GC–MS analyses were performed using a CP 3800-Saturn 2200 gas chromatograph––mass spectrometry instrument (Varian, Middelburg, The Netherlands). The GC analyses were performed using an SP-6890 gas chromatography instrument (Lunan Ruihong, Shandong, China), equipped with a KR-9 capillary column (30 m×0.32 mm×1 μm). The injector and flame ionization detector (FID) temperature were 200 and 280 °C, respectively. The oven temperature was held at 190 °C; N_2 was the carrier gas (1.1 mL min^{-1}). The injected volume was 0.60 μL with the split ratio set at 60:1.

Experimental apparatus

Glycerol chlorination reaction experiments were realized in a self-designed glass apparatus shown in Fig. 1. Glycerol and catalyst were fed into the glass-jacketed reactor, and the external circulation oil bath controller maintained the reaction mixture at the predetermined temperature. Then hydrogen chloride gas, previously dried using a gas dryer, was introduced into the reactor. A porous glass fritter and strong mechanical stirring assured that the gas–liquid interface contacted well. The excess hydrogen chloride gas was fed through a protection bottle and absorbed by alkali liquor in the exit gas absorption bottle. Reaction mixture samples were withdrawn through a valve at the bottom of the reactor for gas chromatographic analysis.

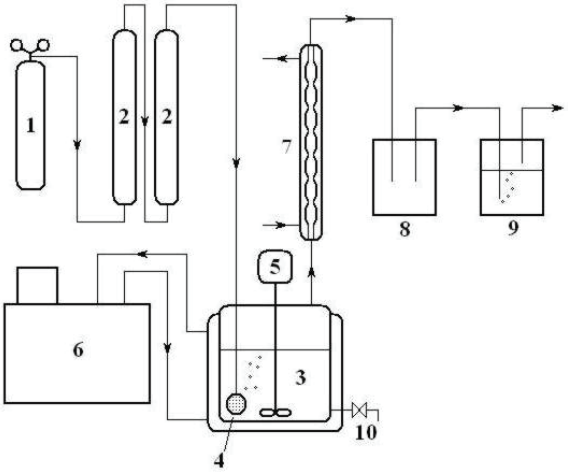


Fig. 1. Schematic diagram of glycerol chlorination reaction apparatus. 1. hydrogen chloride cylinder; 2. gas dryer; 3. reactor; 4. porous fritter; 5. mechanical stirrer; 6. circulation oil bath controller; 7. condenser; 8. protection bottle; 9. exit gas absorber; 10. sampling valve.

RESULTS AND DISCUSSION

The total ion chromatogram of a sample obtained under the optimal chromatographic conditions is shown in Fig. 2. It depicts that there were five components in the glycerol chlorination products and all components in the sample were well separated during 6 min without additional derivatization. These five components were detected with the mass spectrum detector and the mass spectrograms are shown in Fig. 3.

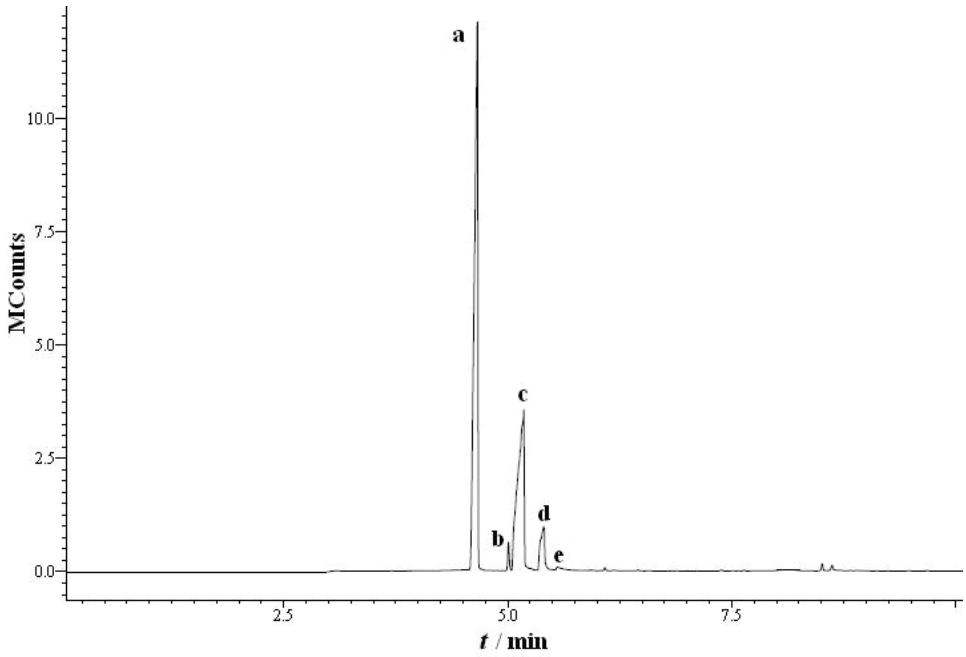


Fig. 2. Total ion chromatogram of the products of glycerol chlorination.

1,3-DCP and 2,3-dichloropropan-1-ol (2,3-DCP) are isomers and, having the same molecular weight, great difficulties are encountered in distinguishing them. Generally, because molecules of alcohols are often fragmented completely under electron impact (EI), the molecular ion peaks of 1,3-DCP and 2,3-DCP can hardly appear in their mass spectrogram. According to the laws of alcohol β-cracking and halide substituent rupture, the molecule of 1,3-DCP may produce a fragment ion with *m*/*z* 79 under EI due to the hydroxyl group linking with the β-carbon, while that of 2,3-DCP may produce an *m*/*z* 62 fragment peak due to the hydroxyl group linking with the α-carbon. On the other hand, *m*/*z* 81 and 64 fragment ion peaks, with one-third of the relative abundance of the *m*/*z* 79 and 62 peaks, could appear next to these two peaks, respectively, because of the existence of the isotope ^{37}Cl in the sample. The possible fragmentation pathways of 1,3-DCP and

2,3-DCP are shown in Fig. 4. The fragment ion peaks *m*/*z* 81 and 79 are both present in the mass spectrogram of component **a** while fragment ion peaks *m*/*z* 64 and 62 are present in the spectrogram of component **b**, Fig. 3. Hence, it can be inferred that component **a** in the total ion chromatogram is 1,3-dichloropropan-2-ol and component **b** is 2,3-dichloropropan-1-ol.

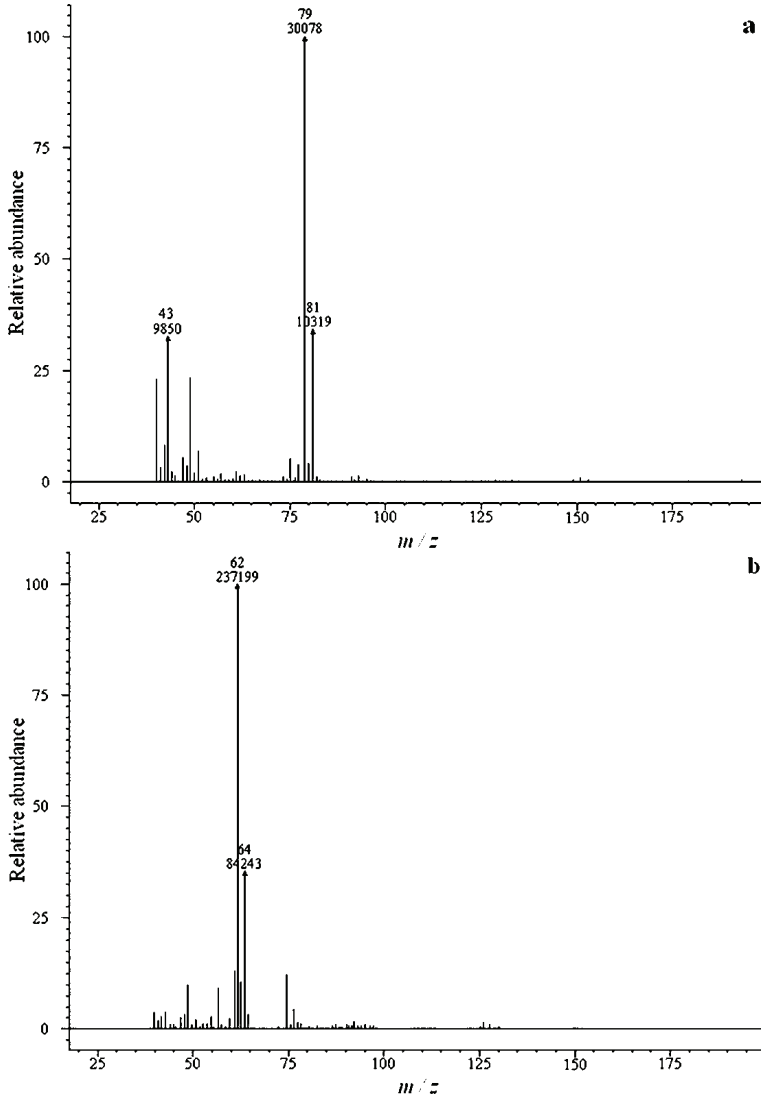


Fig. 3. Mass spectrograms of components **a** and **b**.

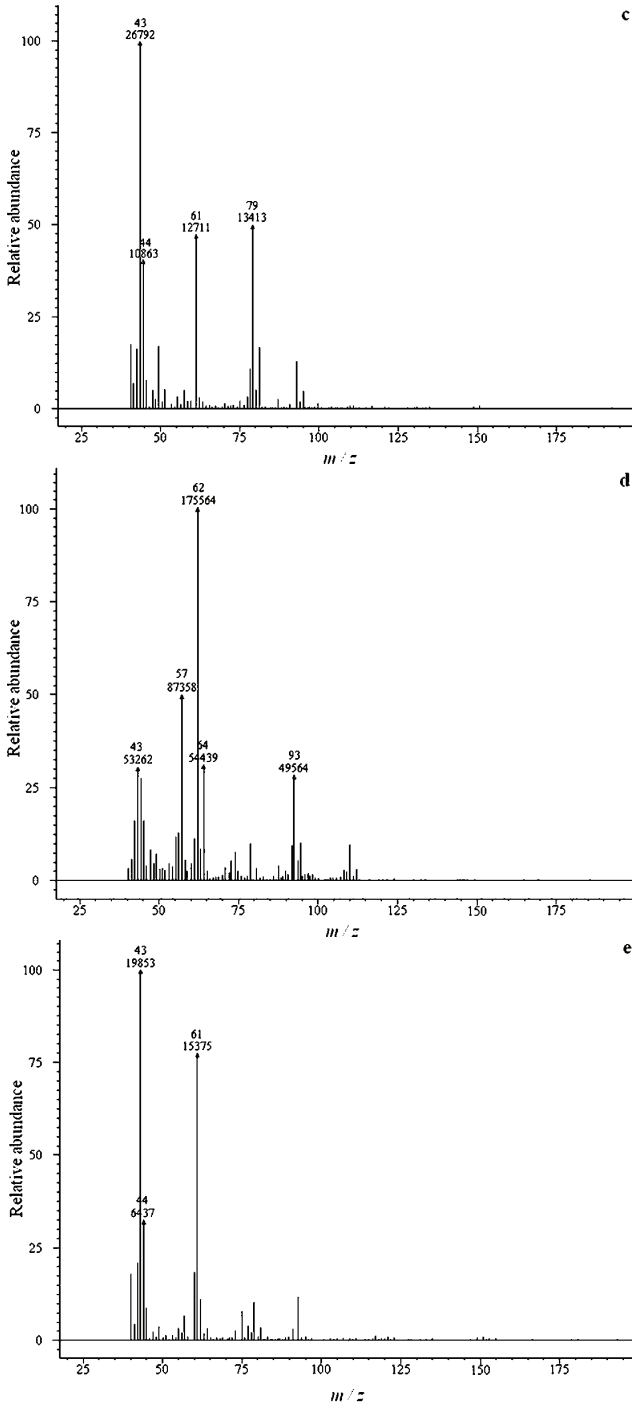


Fig. 3 continued. Mass spectrograms of components **c**, **d** and **e**.

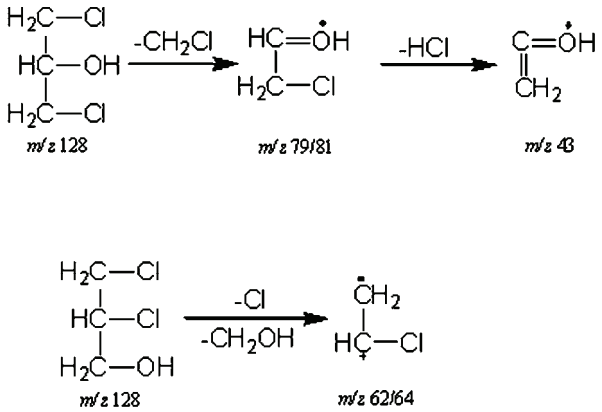


Fig. 4. Fragmentation pathways of 1,3-dichloropropan-2-ol and 2,3-dichloropropan-1-ol under electron impact.

3-MCP and 2-chloro-1,3-propanediol (2-MCP) are also isomers and neither of their molecular ion peaks can appear in the EI mass spectrogram. The molecule of 2-MCP may produce a fragment ion with *m*/*z* 62 under EI due to hydroxyl group and chlorine atom linking with their α-carbon and β-carbon respectively, while that of 3-MCP may produce a *m*/*z* 79 fragment ion due to hydroxyl group and chlorine atom linking with their α-carbon and γ-carbon, respectively, according to the laws of alcohol β-cracking and halide substituent rupture. In addition, *m*/*z* 81 and 64 fragment ion peaks, with one-third of the relative abundance of the *m*/*z* 79 and 62 peaks, may appear next to these two peaks, respectively, also because of the existence of the ^{37}Cl isotope in the sample. The possible fragmentation pathways of 3-MCP and 2-MCP are shown in Fig. 5. The fragment ion peaks *m*/*z* 79 and 81 are both present in the mass spectrogram of component **c** while the fragment ion peaks *m*/*z* 62 and 64 are both present in the mass spectrogram of component **d**. Hence it can be inferred that component **c** in the total ion chromatogram is 3-chloro-1,2-propanediol and component **d** is 2-chloro-1,3-propanediol.

There are three hydroxyl groups in the molecule of glycerol meaning that the molecular ion peak must be absent in its EI mass spectrogram. The molecule of glycerol may produce a fragment ion with *m*/*z* 61 under EI according to the law of alcohol β-cracking. The possible fragmentation pathway of glycerol is shown in Fig. 6. These fragment ion peaks are all present in the mass spectrograms of component **e**. Hence, it can be inferred that component **e** in the total ion chromatogram is glycerol.

Tesser *et al.* indicated that there was no relationship between the acidity strength of a catalysts and its catalytic activity,[15] while Phillipe *et al.* proposed that a variety of carboxylic acid could catalyze the chlorination reaction.[17] In the

present study, different kinds of lower carboxylic acids, such as acetic acid, propanoic acid, malonic acid, succinic acid and adipic acid, were utilized as catalysts in the experiments. A comparison of the catalytic effect of a variety of catalysts is depicted in Fig. 7, from which it can be seen that acetic acid, propanoic acid and adipic acid displayed better catalytic effects that the other investigated catalysts. However, the low boiling point of acetic acid and propanoic acid caused severe volatilization loss of these acids, which lowered the rate of the reaction. To overcome these shortcomings, apidic acid was selected as the chlorination catalyst.

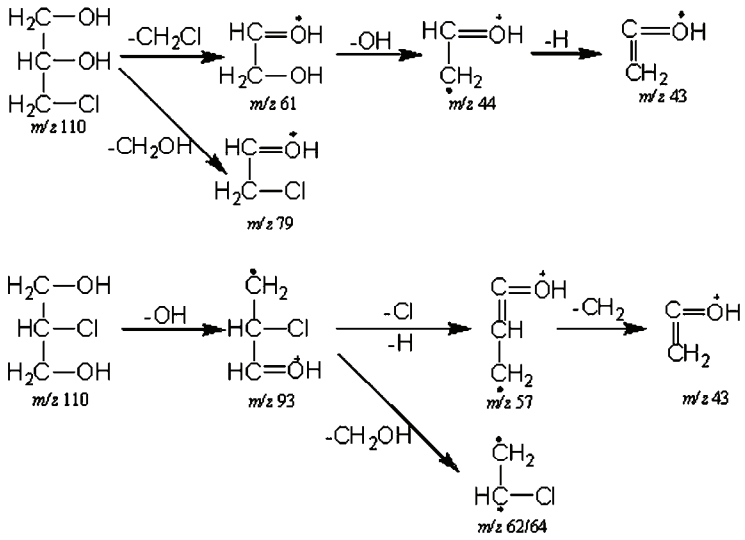


Fig. 5. Fragmentation pathways of 3-chloro-1,2-propanediol and 2-chloro-1,3-propanediol under electron impact.

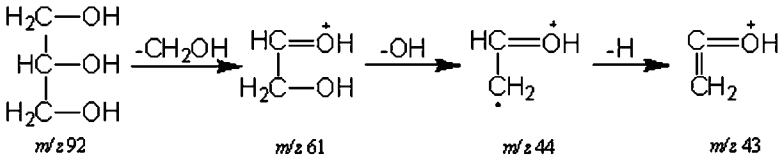
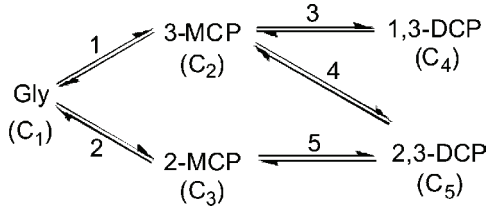


Fig. 6. Fragmentation pathways of glycerol under electron impact.

According to the reaction products glycerol chlorination determined by GC–MS, the net tandem reaction can be schematized in the following manner:



(1)

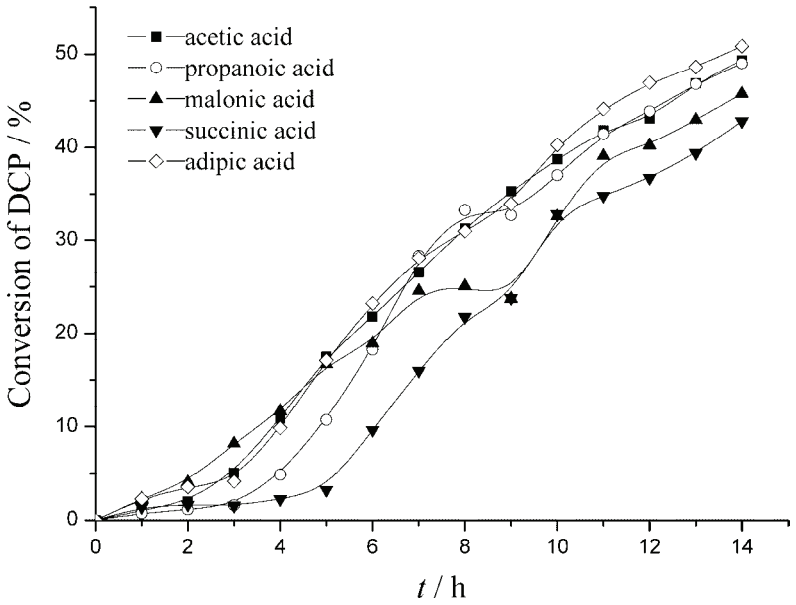
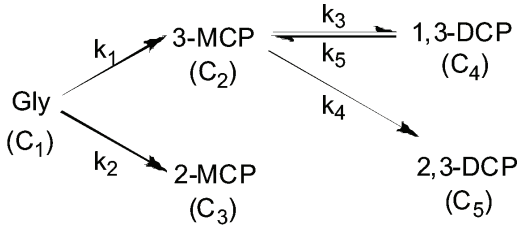


Fig. 7. Comparison of a variety of catalysts on the conversion of dichloropropanol.

The evolution of each component in the reaction product under the optimum condition is depicted in Fig. 8. It can be observed that the concentration of 2-MCP hardly increased when glycerol was still present in the reaction mixture. After a sufficiently long time, the amount of glycerol decreased to a low constant value. Tesser *et al*. considered that conversion of 2-MCP to 2,3-DCP could be neglected, namely reaction path 5 (Eq. (1)) does not occur. Reaction paths 2 and 4 (Eq. (1)) can be considered as being irreversible, due to the low accumulation of 2-MCP and 2,3-DCP throughout the whole reaction process.[15] Moreover, reaction 1 can also be considered as being irreversible because rate of reaction 1 from glycerol to 3-MCP is very high and glycerol can finally be completely converted. According to these hypotheses, the glycerol chlorination reaction model can be modified to the following:



(2)

Thus, the kinetic model can be reduced to the following differential equations:

$$\frac{dc_1}{dt} = -k_1c_1 - k_2c_1;\ \frac{dc_2}{dt} = k_1c_1 - k_3c_2 + k_5c_4 - k_4c_2;\ \frac{dc_3}{dt} = k_2c_1$$
$$\frac{dc_4}{dt} = k_3c_2 - k_5c_4;\ \frac{dc_5}{dt} = k_4c_2 \quad (3)$$

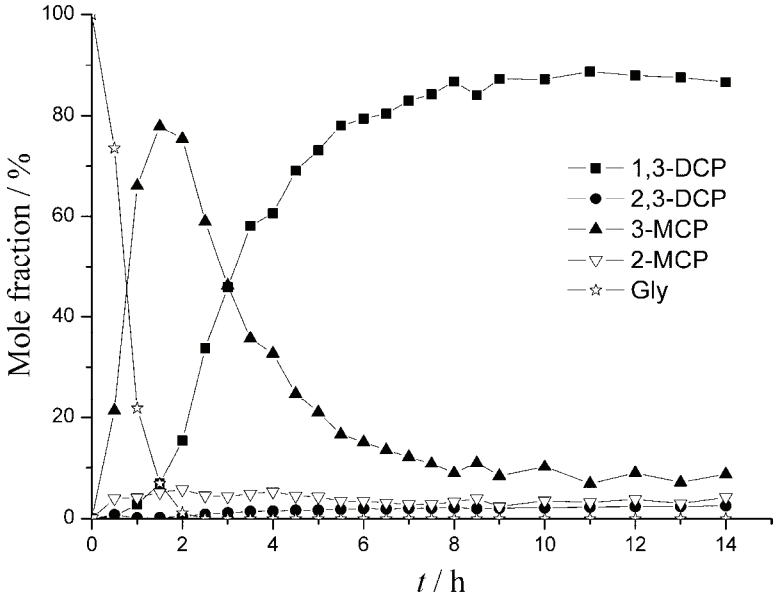


Fig. 8. Evolution of the composition in the glycerol chlorination process under optimum conditions.

The kinetic constants at various temperatures were calculated by non-linear regression in Matlab, based on the kinetic model and the data of the time evolution of the composition, reported in Table I.

TABLE I. Rate constants of the positive reactions at different temperatures

t / °C	$k_1\times10^2$ / min^{-1}	$k_2\times10^4$ / min^{-1}	$k_3\times10^3$ / min^{-1}	$k_4\times10^5$ / min^{-1}
90	1.23	3.16	2.42	3.12
100	1.35	4.59	4.18	8.70
110	2.01	6.59	5.39	11.10
120	2.56	9.07	5.03	11.37

Then, according to the Arrhenius equation:

$$\ln k = -\frac{E_a}{RT} + b \quad (4)$$

the slopes, namely the activation energy of the tandem reactions, were determined by plotting –ln k as the ordinate against 1/RT as the abscissa. The obtained

values were: $E_a(1)$ = 30.7 kJ mol^{-1}, $E_a(2)$ = 41.8 kJ mol^{-1}, $E_a(3)$ = 29.4 kJ mol^{-1} and $E_a(4)$ = 49.5 kJ mol^{-1}. The kinetic constants were then introduced into kinetic equations and the results were in good agreement with experimental data, as shown in Fig. 9, which demonstrates that this kinetic model can predict the chlorination process behavior very well.

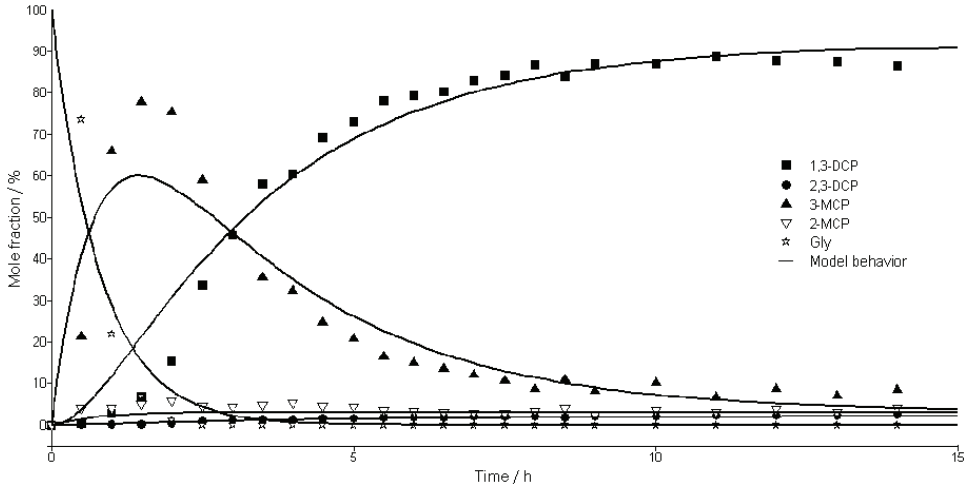


Fig. 9. Comparison between the experimental data and the behavior predicted by the proposed model.

CONCLUSIONS

A convenient and accurate gas chromatography–mass spectrometry method that can simultaneously determine the composition of glycerol chlorination products was first established. The possibility of distinguishing the isomers of monochloropropanediol and dichloropropanol in the reaction products from the mass spectra of the individual products provided the basis for further study of the reaction kinetics and industrial production.

The dynamic behavior of the glycerol chlorination reaction was investigated and a new dynamic model was proposed. According to regression fitting of the experimental data, kinetic equations were obtained and the activation energy of each positive tandem reaction was calculated as follows: $E_a(1)$ = 30.7 kJ mol^{-1}, $E_a(2)$ = 41.8 kJ mol^{-1}, $E_a(3)$ = 29.4 kJ mol^{-1} and $E_a(4)$ = 49.5 kJ mol^{-1}. The fitting curves were in good agreement with the experimental data.

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ИЗВОД

ИСПИТИВАЊЕ КИНЕТИКЕ И МЕХАНИЗМА РЕАКЦИЈЕ ХЛОРОВАЊА ГЛИЦЕРОЛА ГАСНО–МАСЕНОМ СПЕКТРОМЕТРИЈОМ

XIUQUAN LING[1], DINGQIANG LU[1,2], JUN WANG[1], MINGXIN LIANG[1], SHUMIN ZHANG[1], JIANHUI CHEN[1] и PINGKAI OUYANG[1]

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Као примарни споредни производ у производњи биодизела, глицерол се може употребити за синтезу важне супстанце епихлорхидрина, који настаје као интермедијерни производ у процесу хлоровања глицерола. Мада се тај процес користи у индустријским условима, мала пажња је била поклоњена анализи и сепарацији хлорираних производа реакције. У овом раду је испитана кинетика и механизам реакције и описан одговарајући и прецизан метод одређивања производа реакције. Применом гасно–масене спектрометрије утврђено је да производ реакције садржи 1,3-дихлоро 2-пропанол, 2,3-дихлоро 1-пропанол, 3-хлоро-1,2--пропандиол, 2-хлоро-1,3-пропандиол и глицерол. Због високе тачке кључања и добрих каталитичких особина адипинска киселина се показала као најбољи катализатор у овој реакцији. Предпостављен је механизам и развијен је нови кинетички модел ове реакције. Фитовањем експерименталних података добијене су следеће вредности за енергије активације појединачних ступњева: 30,7, 41,8, 29,4 и 49,5 kJ mol^{-1}. Овај рад, разјашњавајући кинетику и механизам процеса, поставља теоријску основу за инжењеризацију овог процеса.

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