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Determination of kinetic parameters of dehydrochlorination of dichloropropanol in a microreactor

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HIGHLIGHTS

- The kinetics of dehydrochlorination of dichloropropanol is studied in a microreactor.
- 2,3-Dichloro-1-propanol is much less reactive than 1,3-dichloro-2-propanol.
- Rate constants are determined in the temperature range of 50–80 °C.
- The kinetics is found to be first order to [OH^-] and second order to [DCP].
- The activation energy is 150 (±10) kJ mol^{-1} and the pre-exponential factor is 1.61×10^{25}.

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ABSTRACT

The reaction kinetics of dehydrochlorination of dichloropropanol (including 1,3-dichloro-2-propanol and 2,3-dichloro-1-propanol) is investigated with a microchemical system, which is constructed with a micromixer, a micro-tube and a microneutralizer. The reaction starts up by mixing dichloropropanol solution and sodium hydroxide solution in the micromixer, proceeds in the following micro-tube for a residence time strictly controlled to several seconds, and quenches in the microneutralizer. The results show that 2,3-dichloro-1-propanol is much less reactive than 1,3-dichloro-2-propanol. Rate constants of the dehydrochlorination reaction (2,3-dichloro-1-propanol) are determined in the temperature range of 50–80 °C. The reaction kinetics is found to be first order with respect to hydroxyl ion concentration and second order to dichloropropanol concentration. The activation energy is 150 (±10) kJ mol^{-1} and the pre-exponential factor is 1.61×10^{25}. Compared with earlier reports on the kinetics of this reaction, this microchemical system provides information much closer to what the intrinsic kinetics determines, showing distinct values for reaction mechanism understanding and process intensification in further work.

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1. Introduction

Epichlorohydrin (ECH) is an important raw material for producing epoxy resins, elastomers and synthetic glycerin [1,2]. Several routes are well known for epichlorohydrin manufacture [3–5], and propylene and chlorine are mainly used as primary raw materials. The dominant process is a multi-step process, as shown in Fig. 1. This process mainly includes chlorination of propylene at a high temperature to allyl chloride, chlorohydrination of allyl chloride with chlorine in water to dichloropropanol (DCP) and conversion of DCP to ECH in alkali solution. Recently, as glycerin is increasingly supplied as a by-product of biodiesel manufacture, a great attention is focused on the development of new chlorination process from glycerol [6–11]. This two-step process, shown in Fig. 2, directly prepares DCP from glycerol and gets ECH via the same dehydrochlorination or saponification process.

The dichloropropanol formed in the commercial route is in the form of a mixture of two isomers: 1,3-dichloro-2-propanol (1,3-DCP, 30%) and 2,3-dichloro-1-propanol (2,3-DCP, 70%). The dehydrochlorination conditions of both isomers cannot be optimized at the same time because the reaction rates of the isomers are quite different. According to the literatures [12,13], the reaction rate of 1,3-DCP is about 20 times faster than that of 2,3-DCP. Thus, a long residence time is needed to ensure the sufficient conversion of major 2,3-DCP, which results in an increase of side reaction of epichlorohydrin hydrolysis. The improvement in the yield of epichlorohydrin is naturally limited. Therefore, the determination of kinetic parameters is important to optimize the operating conditions, design reactor and improve the process control. Some work has been devoted to the kinetics. Carrà et al. [12] determined the kinetic parameters of 1,3-DCP and 2,3-DCP in an

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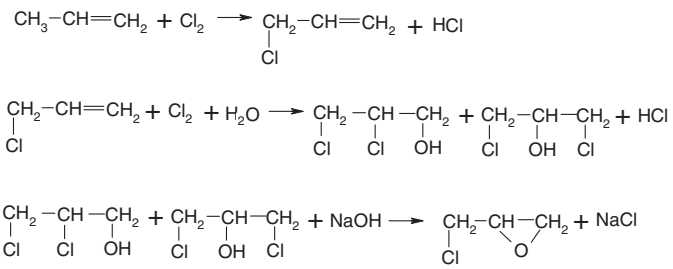


Fig. 1. The dominant commercial route for producing epichlorohydrin from propylene and chlorine.

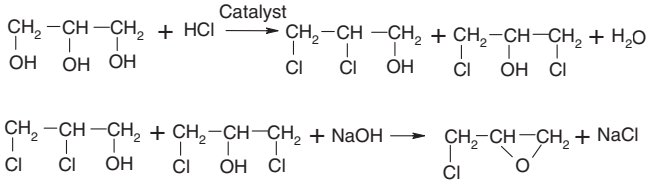


Fig. 2. The route for producing epichlorohydrin from glycerol.

aqueous solution containing an excess of $Ca(OH)_2$ and offered a kinetic model of the overall system using the techniques of potentiometry and gas chromatography. Ma et al. [14] studied the kinetics of dehydrochlorination of DCP (mainly 1,3-DCP) and the side reaction of ECH hydrolysis. The results indicate that both two reactions can be considered as second order reactions. But all the experiments are performed in stirred batch reactor in which the poor mixing performance may mislead the kinetic model based on the assumption of an ideal batch reactor especially when the temperature is higher. We can find a deviation of the model from the data when the temperature is higher than 50 °C. As a result, more work should be done to describe the process more clearly.

Microreactors are attractive for performing kinetics measurements for enhanced reagent mixing, precise control over reaction temperature and residence time, minute reagents consumption [15]. Thus, more accurate kinetic parameters can be extrapolated, which would otherwise be difficult using a batch flask. They have been used to characterize kinetics at Diels–Alder reaction [16], synthesis of sodium nitrotetrazolate (NaNT) [17] and fast exothermic pre-mixing reaction [18].

In this work, a microchemical system, including a micromixer, a micro-tube and a microneutralizer, was designed to study the kinetics of dehydrochlorination of dichloropropanol. The objective of this work is to improve the accuracy of kinetic investigations and establish a model approaching intrinsic kinetics for reaction mechanism understanding and process intensification. The dichloropropanol solution mixed with sodium hydroxide solution in the micromixer and the reaction proceeded in the micro-tube connecting directly to the micromixer. The residence time was strictly controlled to several seconds with the quenching effect of the microneutralizer. The reaction kinetics of dehydrochlorination of 2, 3-dichloro-1-propanol, including the order of the reaction, the pre-exponential factor and activation energy of the rate constant, were determined in the presence of caustic soda.

2. Materials and methods

2.1. Chemicals

1,3-dichloro-2-propanol (1,3-DCP) ($C_3H_6Cl_2O$, 99%) and 2,3-dichloro-1-propanol (2,3-DCP) ($C_3H_6Cl_2O$, 97%) were purchased from J&K Scientific Ltd. (Beijing); Sodium dihydrogen phosphate dehydrate ($NaH_2PO_4{\cdot}2H_2O$, 99.5%), disodium hydrogen phosphate anhydrous ($Na_2HPO_4{\cdot}12H_2O$, 99.0%) from Tianjin Guangfu Fine Chemical Research Institute. Epichlorohydrin (ECH) (C_3H_5ClO) and sodium hydroxide (NaOH) were all of analytical grade and acquired from Sinopharm Chemical Reagent Beijing Co., Ltd.

2.2. Experimental setup

A schematic overview of the microchemical system is shown in Fig. 3. The reactants were delivered by metering pumps (Beijing Satellite Co. Ltd.) from glass bottles and separately pumped into stainless steel capillaries with an inner diameter of 1.4 mm and an external diameter of 2 mm, representing the feed stream tubes. The feed streams were preheated to the reaction temperature and then mixed in a micro-sieve dispersion mixer (316 stainless steel). The structure and the mixing performance have been described in literatures [19,20]. The dispersion aperture is square and 0.2 mm in the side length. The microchannel in the mixer is 10 mm in length, 0.4 mm in width and 0.6 mm in height. A stainless steel micro-tube with an inner diameter of 1.4 mm and an external diameter of 2 mm is connected directly downstream to the micromixer to control the residence time. The reaction time could be controlled accurately by changing the length of the micro-tube. The preheating zone, the mixer and the micro-tube were immerged in a water bath. When leaving the reaction zone, a microneutralizer was designed to quench the reaction. An excessive amount of phosphate buffer solution (pH = 7.0) was pumped into the reacting system and changed the pH of reacting mixture to about 7.0. Hydroxyl ion was consumed and dehydrochlorination was terminated. The samples were collected at the outlet after the microneutralizer for determining the DCP conversion. To avoid the hydrolysis of ECH in water, the samples were stored for less than 2 h in an ice water bath before analysis.

2.3. Sample analysis

The samples were collected directly from the outlet of the microneutralizer. The samples were diluted and measured by gas chromatography (Shimadzu GC-2014) with a flame ionization detector under following conditions: the injection temperature, 220 °C; the column temperature, 70–220 °C, 30 °C/min; the detector temperature, 280 °C. The sample volume for all analysis was 2 μL. The dichloropropanol conversion X is calculated by the following equations:

$$X = 1 - \frac{W_{DCP} \times M_{pro}}{F_{DCP}} \quad (1)$$

where W_{DCP} (%) is the mass fraction of DCP in the sample, M_{pro} (g) is the mass of the collected sample and F_{DCP} (g) is the feeding mass of DCP calculated with the feeding rate of DCP solution and the sam-

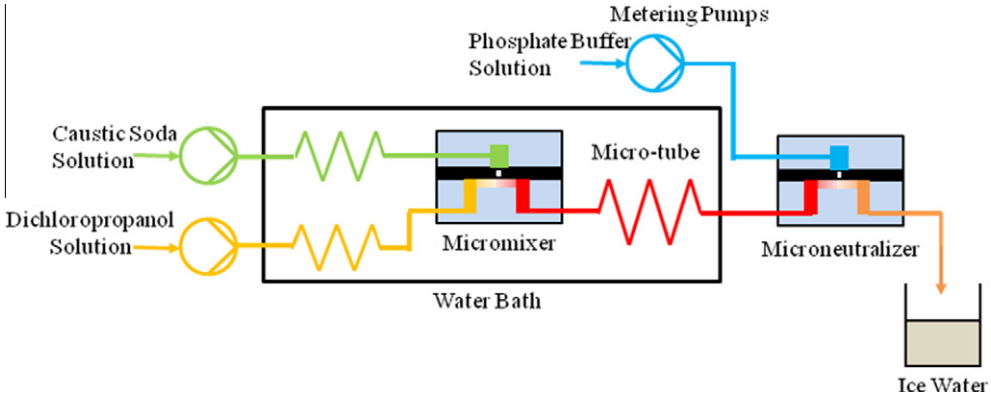


Fig. 3. The schematic overview of the microchemical system.

pling time. By this method, the conversion (measured in percentage) is determined within a measurement error of 0.5%.

3. Results and discussion

3.1. Different reaction rates of 1,3-DCP and 2,3-DCP in the microchemical system

Experimental conditions: 1,3-DCP and 2,3-DCP solution (1 wt.% each): 10 ml/min; NaOH solution (0.65 wt.%): 5 ml/min; phosphate buffer solution (pH = 7.0, 0.5 mol/L): 5 ml/min. The molar ratio of OH^- to DCP was 1.05 and the residence time of 1,3-DCP and 2,3-DCP were 2 s and 10 s, respectively. The micro-tubes for 1,3-DCP and 2,3-DCP were 0.32 m and 1.62 m, respectively.

Fig. 4 shows the effect of temperature on the conversion of 1,3-DCP and 2,3-DCP within a range of 35–85 °C at the residence time of 2 s and 10 s respectively. The conversion of 1,3-DCP can reach about 85% at 35 °C and 2,3-DCP of 14% at 55 °C in the microchemical system while the conversion of 1,3-DCP and 2,3-DCP at the same temperature are only about 10% and near zero respectively in the literature [12]. The results indicate that the microchemical system can improve the reaction rate greatly due to the excellent mixing performance and enhanced mass transfer characteristics. When the temperature increases to 45 °C or higher, 1,3-DCP conversion reaches to nearly 100% while 2,3-DCP conversion increases quickly from about 14% to 80% when the temperature is increased to 85 °C. It shows the fact that 2,3-DCP is much less reactive than 1,3-DCP. As 2,3-DCP is the majority in the DCP solution in the conventional process, designing the residence time should mainly consider the reaction rate of 2,3-DCP. The minority of 1,3-DCP can be quickly consumed in the early stage of dehydrochlorination process. As a result, determination of kinetic parameters of 2,3-DCP is especially important to optimize the reaction process.

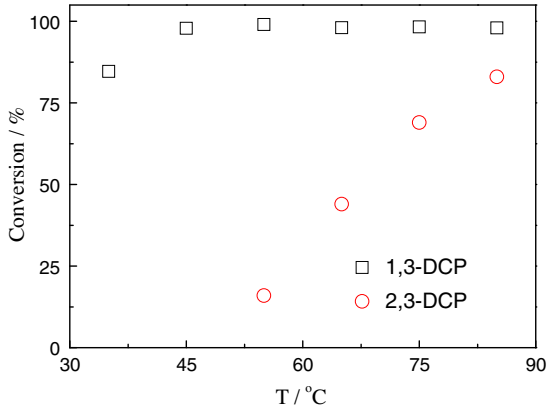
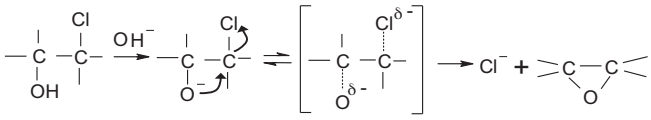


Fig. 4. Conversion of 1,3-DCP and 2,3-DCP at different temperature.

The dehydrochlorination reaction occurs according to an internal nucleophilic substitution (S_N2) mechanism [21,22], as shown in Eq. (2). In the reaction, the internal nucleophile ($-O^-$) attacks the carbon with the good leaving group, forming a C–O bond and breaking the C–Cl bond.



(2)

The reactivity of dichloropropanol is strongly affected by the position of substituent groups and on their electron withdrawing character. 1,3-DCP has two chlorine atoms which can be attacked by the nucleophile while only one corresponding chlorine atom in 2,3-DCP. Furthermore, the inductive effects of both the chlorine atoms of 1,3-DCP favor the hydrogen mobility of the hydroxyl group. On the contrary, in 2,3-DCP, the adjacent chlorine atoms interact with each other, reducing the overall effect on the hydrogen mobility. This may be the main reason why 1,3-DCP is more reactive than 2,3-DCP.

3.2. Modelling of the reaction kinetics of 2,3-DCP dehydrochlorination in the microchemical system

3.2.1. The reaction order of DCP

Experimental conditions: 2,3-DCP solution (0.4 wt.%): 10 ml/min; NaOH solution (4 wt.%): 3.1 ml/min; phosphate buffer solution (pH = 7.0, 0.5 mol/L): 15 ml/min. The molar ratio of OH^- to DCP was 10 and the reaction temperature was 50 °C. The residence time was varied by changing the length of the reaction tube (0.72–5.54 m).

Fig. 5a shows the trend of conversion of 2,3-DCP at 50 °C. It can reach about 70% conversion at a residence time of 40 s. The conceivable rate equation of the dehydrochlorination reaction can be written as follows:

$$r = -d[\mathrm{DCP}]/dt = k[\mathrm{DCP}]^{\alpha}[\mathrm{OH}^-]^{\beta} \quad (3)$$

where [DCP] and $[OH^-]$ are the concentrations of DCP and OH^-, respectively. For determination of the DCP order, initial concentration of OH^- is 10 times of initial concentration of DCP. And then the rate law can be written as:

$$r = k[\mathrm{DCP}]^{\alpha}[\mathrm{OH}^-]^{\beta} \approx k_{\varphi}[\mathrm{DCP}]^{\alpha} \quad (4)$$

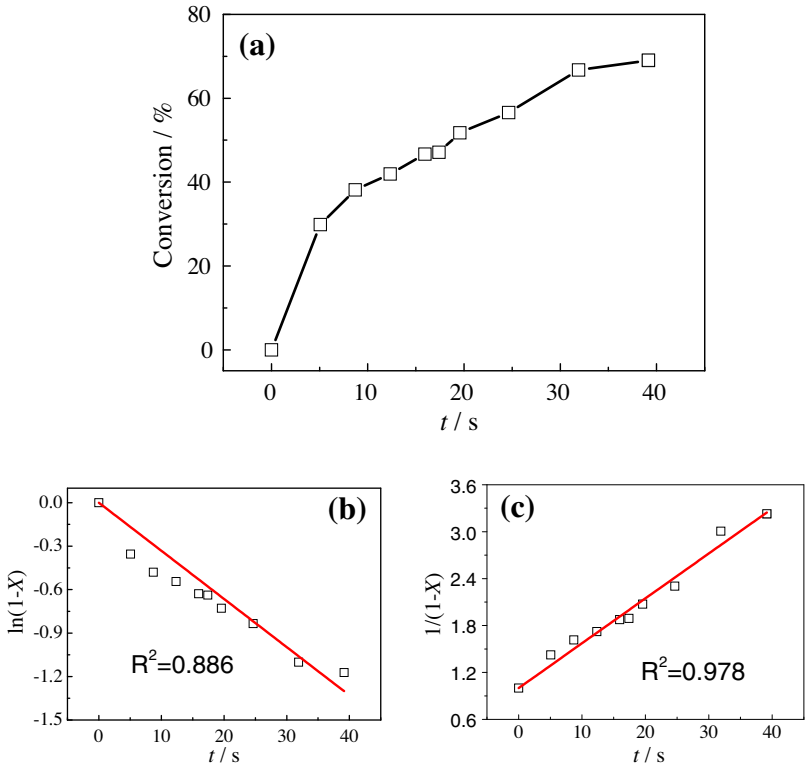


Fig. 5. (a) Conversion of 2,3-DCP versus time at 50 °C. (b) Plot of $\ln(1 - X)$ versus time. (c) Plot of $1/(1 - X)$ versus time.

If the order of DCP is first, the rate law is

$$r = -\frac{dc}{dt} = c_0\frac{dX}{dt} = k_\varphi[\mathrm{DCP}] = k_\varphi c_0(1 - X) \quad (5)$$

where X is the conversion of DCP and c_0 is the initial concentration of DCP. This equation can be solved by integration as

$$\ln(1 - X) = -k_\varphi t \quad (6)$$

So the plot of $\ln(1 - X)$ versus t should be a straight line that passes through the origin. Similarly, Eq. (7) can be gained if the order of DCP is second. The plot of $1/(1 - X)$ versus t should also be a straight line.

$$1/(1 - X) = 1 - k't \quad (7)$$

Fig. 5b and c shows the linear fitting results of $\ln(1 - X)$ versus t and $1/(1 - X)$ versus t respectively. The fitting parameters of correlation coefficient $R^2 = 0.978$ when the order of DCP is second contrast to that of 0.886 when the order of DCP is first and a obvious deviation between the data and the fitting line have been observed in Fig. 5b. The results mean that the kinetic model of second-order with respect to DCP concentration seems more suitable to represent the reaction. Meanwhile, those experimental results in previous reports on the reaction kinetics of DCP dehydrochlorination were usually described as a model of first-order with respect to DCP concentration [12,14]. As mentioned before, the dehydrochlorination process of DCP could be regarded as an internal nucleophilic substitution (SN_2) mechanism as shown in Eq. (2) and the kinetics of DCP should be first-order to [DCP]. But for 2,3-DCP, adjacent chlorine atoms interact with each other, reducing the overall effect on the hydrogen mobility and the internal nucleophile (–O–) could only attack 2-C. Also, it is really hard for the internal nucleophile (–O–) to attack 2-C due to the space effect [14]. We guess there is a bimolecular nucleophilic substitution between two DCP molecules and it is much easier for the nuclephile (–O–) in one molecule to attack 2-C in the other molecule. Maybe this is an explanation for the results that the kinetics is second-order to [DCP]. However, more work needs to be done to prove the assumption, such as changing the starting 2,3-DCP concentration.

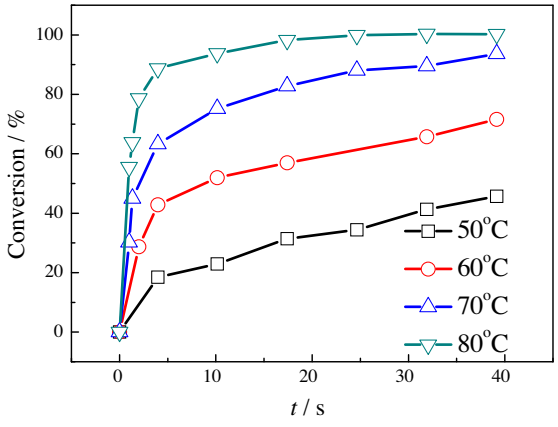


Fig. 6. Conversion of 2,3-DCP versus time at the temperature range of 50–80 °C. Experimental conditions: 2,3-DCP solution (1 wt.%): 10 ml/min; NaOH solution (2 wt.%): 3.1 ml/min; phosphate buffer solution (pH = 7.0, 0.5 mol/L): 10 ml/min. The molar ratio of OH^- to DCP was 2. The residence time was varied by changing the length of the reaction tube (0.14–5.54 m).

3.2.2. The reaction order of hydroxyl ion

Fig. 6 shows the trend of conversion versus time for the dehydrochlorination reaction of 2,3-DCP at the temperature range of 50–80 °C. The results indicate that the reaction rate increases as the temperature increases. Nearly 100% conversion can be reached with a residence time of 20 s at 80 °C. The order of hydroxyl ion was usually thought to be first. Here we adopt the kinetic model

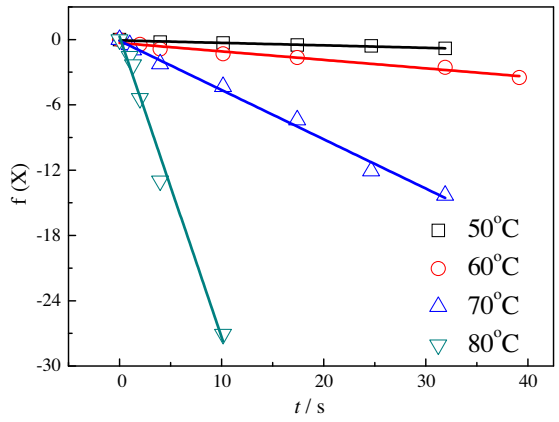


Fig. 7. Plot of $f(X)$ versus time for the reaction at the temperature range of 50–80 °C.

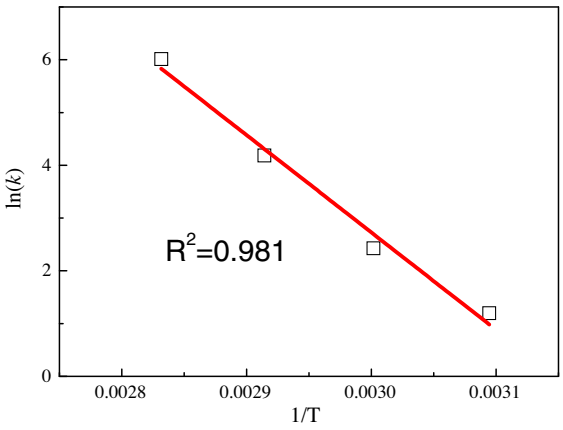


Fig. 8. Plot of ln (k) versus $1/T$ for the reaction.

Table 1
The comparison of correlation coefficients R^2 of fitting the experimental data with two kinetic models.

Temperature (°C)	50	60	70	80
$r = k[DCP]^2[OH^-]$	0.977	0.971	0.996	0.990
$r = k[DCP][OH^-]$	0.803	0.734	0.889	0.946

Table 2
The fitting parameters of the plot of $f(X)$ versus time.

Temperature (°C)	50	60	70	80
Slope	−0.0228 ± 0.002	−0.0779 ± 0.006	−0.45 ± 0.02	−2.8 ± 0.2
k^a (L^3/mol^2 s)	3.3 ± 0.3	11.3 ± 0.9	66 ± 2	410 ± 20

[a] $k = -\text{slope}/(c_{10}c_{20}) = -\text{slope}/0.00688$.

of second-order with respect to [DCP] and first-order with respect to [OH^-] to represent the experimental data reported in Fig. 6. The rate law is as follows:

$$r = k[DCP]^2[OH^-] \tag{8}$$

This equation can be solved by integration as

$$f(X) = -\frac{1}{1-a} \times \frac{X}{1-X} + \frac{a}{(1-a)^2} \ln\left(\frac{1-aX}{1-X}\right) = -k \times c_{10} \times c_{20} \times t \tag{9}$$

where c_{10} is the initial concentration of DCP and c_{20} is the initial concentration of OH^-; a is equal to c_{10}/c_{20}. So the plot of $f(X)$ versus t should be a straight line that passes through the origin. Fig. 7 shows the plot of $f(X)$ versus time at different temperatures according to the data in Fig. 6. When the conversion is close to 100%, a little change in the conversion would bring a large difference in the Fig. 7. Because of the measure error, we have deleted the corresponding results in Fig. 7 when the conversion is close to 100% in Fig. 6. Table 1 shows the correlation coefficient R^2 of fitting the experimental data with two different kinetic models in the range 50–80 °C. The good linearity of the curves indicates that the third order kinetic model is feasible to represent the kinetics of 2,3-DCP.

3.2.3. The pre-exponential factor and activation energy of the rate constant

The values of k at different temperatures are listed in Table 2 and the plot of ln (k) versus $1/T$ is shown in Fig. 8. ln (k) decreases linearly with $1/T$ and, therefore, fits well to the Arrhenius equation:

$$\ln k = \ln A - \frac{E_a}{RT} \tag{10}$$

where A is the pre-exponential factor, Ea is the activation energy, R is the universal gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature. The fitting parameters from this linear plot of correlation coefficient R^2 = 0.981 indicate that the activation energy Ea is 150 (±10) kJ mol^{-1} and the pre-exponential factor A is 1.61×10^{25}. It seems that the activation energy is a little high for the reaction. As mentioned before, 2,3-DCP is less reactive than 1,3-DCP because of the inductive effect and the space effect. That means the activation energy of 2,3-DCP would be higher than that of 1,3-DCP. The fact is substantiated by the results in the literature [12]. In the literature [14], the activation energy of 1,3-DCP (40–60 °C) is 123 kJ mol^{-1}. Therefore the results that activation energy of 2,3-DCP is 150 kJ mol^{-1} in our work seems reasonable.

The kinetic parameters of dehydrochlorination of 2,3-DCP are important for optimizing the operating conditions and improving the process control. For an example, we can model the overall process including the dehydrochlorination (1,3-DCP and 2,3-DCP) and ECH hydrolysis and enhance the process in microreactors to improve the yield in the further work.

4. Conclusion

In this study, a microchemical system has been successfully applied to investigate the kinetics of dehydrochlorination of dichloropropanol in caustic soda. The results show that both the dehydrochlorination processes of 2,3-DCP and 1,3-DCP can be strongly intensified due to the enhanced mass transfer rate, and 2,3-DCP with far less reactivity than 1,3-DCP is absolutely crucial for a sufficient conversion. The reaction rate is found to be first order with respect to hydroxyl ion concentration and second order to dichloropropanol concentration. The activation energy of the rate constant is 150 (±10) kJ mol^{-1} and the pre-exponential factor is 1.61×10^{25}. Compared with earlier reports on the kinetics of this reaction, this microchemical system provides information much closer to what the intrinsic kinetics determines, showing distinct values for reaction mechanism understanding and process intensification in further work.

Acknowledgements

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References

[1] J.W. Bijsterbosch, A. Das, F.P.J.M. Kerkhof, Clean technology in the production of epichlorohydrin, J. Cleaner Prod. 2 (1994) 181–184.
[2] J.J. Baldwin, A.W. Raab, K. Mender, B.H. Arison, D.E. McClure, Synthesis of (R)- and (S)-epichlorohydrin, J. Org. Chem. 43 (1978) 4876–4878.
[3] L. Wang, Y. Liu, W. Xie, H. Zhang, H. Wu, Y. Jiang, M. He, P. Wu, Highly efficient and selective production of epichlorohydrin through epoxidation of allyl chloride with hydrogen peroxide over Ti-MWW catalysts, J. Catal. 246 (2007) 205–214.
[4] W. Kim, C. Yun, Y. Kim, J. Park, S. Park, K.T. Jung, Y.H. Lee, S.H. Kim, Modeling of a tubular reactor producing epichlorohydrin with consideration of reaction kinetics and deactivation of titanium silicate-1 catalyst, Ind. Eng. Chem. Res. 50 (2011) 1187–1195.
[5] N. Nagato, H. Mori, K. Maki, R. Ishioka, Process for production of epichlorohydrin, Pat. US 4,634,784, 1987.
[6] E. Santacesaria, R. Tesser, M.D. Serio, L. Casale, D. Verde, New process for producing epichlorohydrin via glycerol chlorination, Ind. Eng. Chem. Res. 49 (2010) 964–970.
[7] S.H. Lee, D.R. Park, H. Kim, J. Lee, J.H. Jung, S.Y. Woo, W.S. Song, M.S. Kwon, I.K. Song, Direct preparation of dichloropropanol (DCP) from glycerol using heteropolyacid (HPA) catalysts: a catalyst screen study, Catal. Commun. 9 (2008) 1920–1923.
[8] R. Tesser, E. Santacesaria, M.D. Serio, G.D. Nuzzi, V. Fiandra, Kinetics of glycerol chlorination with hydrochloric acid: a new route to α, γ-dichlorohydrin, Ind. Eng. Chem. Res. 46 (2007) 6456–6465.
[9] Z.H. Luo, X.Z. You, H.R. Li, A kinetic model for glycerol chlorination in the presence of acetic acid catalyst, Korean J. Chem. Eng. 27 (2010) 66–72.
[10] Z.H. Luo, X.Z. You, H.R. Li, Direct preparation kinetics of 1,3-dichloro-2-propanol from glycerol using acetic acid catalyst, Ind. Eng. Chem. Res. 48 (2009) 446–452.
[11] Z.H. Luo, X.Z. You, J. Zhong, Design of a reactive distillation column for direct preparation of dichloropropanol from glycerol, Ind. Eng. Chem. Res. 48 (2009) 10779–10787.
[12] S. Carrà, E. Santacesaria, M. Morbidelli, P. Schwarz, C. Divo, Synthesis of epichlorohydrin by elimination of hydrogen chloride from chlorohydrins. 1. Kinetic aspects of the process, Ind. Eng. Chem. Process Des. Dev. 18 (1979) 424–427.
[13] S. Carrà, E. Santacesaria, M. Morbidelli, P. Schwarz, C. Divo, Synthesis of epichlorohydrin by elimination of hydrogen chloride from chlorohydrins. 2. Simulation of the reaction unit, Ind. Eng. Chem. Process Des. Dev. 18 (1979) 428–433.
[14] L. Ma, J.W. Zhu, X.Q. Yuan, Q. Yue, Synthesis of epichlorohydrin from dichloropropanols kinetics aspects of the process, Chem. Eng. Res. and Des. (Trans IChemE) 85 (2007) 1580–1585.
[15] R.L. Hartman, K.F. Jensen, Microchemical systems for continuous-flow synthesis, Lab Chip 9 (2009) 2495–2507.
[16] J.P. McMullen, K.F. Jensen, Rapid determination of reaction kinetics with an automated microfluidic system, Org. Process Res. Dev. 15 (2011) 398–407.
[17] N. Zaborenko, E.R. Murphy, J.G. Kralj, K.F. Jensen, Synthesis and kinetics of highly energetic intermediates by micromixers: direct multistep synthesis of sodium nitrotetrazolate, Ind. Eng. Chem. Res. 49 (2010) 4132–4139.
[18] K. Wang, Y.C. Lu, Y. Xia, H.W. Shao, G.S. Luo, Kinetics research on fast exothermic reaction between cyclohexanecarboxylic acid and oleum in microreactor, Chem. Eng. J. 169 (2011) 290–298.
[19] J.S. Zhang, K. Wang, Y.C. Lu, G.S. Luo, Characterization and modeling of micromixing performance in micropore dispersion reactors, Chem. Eng. Process 49 (2010) 740–747.
[20] J.S. Zhang, K. Wang, Y.C. Lu, G.S. Luo, Beckmann rearrangement in a microstructured chemical system for the preparation of ε-caprolactam, AIChE J. 58 (2012) 925–931.
[21] S. Patai, The Chemistry of Functional Groups, Interscience Publishers, Wiley, New York, USA, 1967.
[22] A. Weissberger, The Chemistry of Heterocyclic Compounds, vol. 180, Interscience, New York, USA, 1964. 210.