SYNTHESIS OF EPICHLOROHYDRIN FROM DICHLOROPROPANOLS
Kinetic Aspects of the Process

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Abstract: The reactions involved in the industrial production of epichlorohydrin from dichloropropanols (DCP, including 1,3-dichloro-2-propanol and 2-3-dichloro-1-propanlol) have been kinetically investigated. The kinetics of dehydrochlorination of DCP has been studied in the presence of caustic soda, by potentiometric techniques. The kinetic parameters of the reactions have been determined. The epichlorohydrin hydrolysis has been studied by measuring the decrease of the reagents during the time using titration. The whole study indicate that both dehydrochlorination and hydrolysis reaction can be considered as second order kinetic reaction. It is also indicated that the kinetic constant for dehydrochlorination reaction is far bigger than that for hydrolysis reaction in the same conditions.

Keywords: dichloropropanol; epichlorohydrin; kinetics; dehydrochlorination; hydrolysis; activation energy.

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DOI: 10.1205/cherd07061

0263–8762/07/
$30.00 + 0.00

Chemical Engineering Research and Design

Trans IChemE,
Part A, December 2007

INTRODUCTION

Originally, epichlorohydrin(EPCH; IUPAC name:1-chloro-2,3-epoypropane) was formed by Berthelot in 1854 (Berthelot and Luca, 1856), and by Clarke and Hartman (1941), using caustic soda for hydrolysis with the product of the reaction happened between hydrogen chloride and crude glycerol.

$$C_3H_8O_3 + HCl \xrightarrow{\text{catalyst}} C_3H_6Cl_2O + H_2O \qquad (1)$$

$$C_3H_6Cl_2O + NaOH \rightarrow C_3H_5ClO + NaCl + H_2O \qquad (2)$$

At present, energy source shortages caused obtaining chemical materials from biomass, and it was successful. Because of the high price of the petroleum, the glycerol process of producing EPCH has lower cost than the synthesis from petroleum products. And now, the process of producing EPCH from glycerol was considered by many big chemical groups, such as SOLVAY, DOW, DUPONT, SHANG HAI HUAYI GROUP, and so on. Then, EPCH will be mainly prepared in industry from the DCP, followed by dehydrochlorination of DCP, according to equations (1) and (2) (Braun, 1932, 1943; Fairbourne *et al*., 1930; Horsley, 1965):

The basic medium necessary for the second reaction can be obtained by using a caustic soda solution, afforded by Huayi Group, Shanghai. Together with the dehydrochlorination reaction, hydrolysis always occurs, according to the scheme:

$$EPCH + NaOH + H_2O \rightarrow C_3H_8O_3 + NaCl \qquad (3)$$

But the hydrolysis reaction lowers the yields; EPCH must be removed as quickly as possible from the reaction environment. The dehydrochlorination reaction is performed in a distillation column, and EPCH is flashed out with stream to shorten the contact time to prevent hydrolysis.

Designing suitable reactors for dehydrochlorination reaction and the distillation column and choosing the optimal operating conditions require the determination of kinetic parameters for the reactions involved in the process and the evaluation of vapour–liquid equilibrium data. But both the kinetics of dehydrochlorination and hydrolysis in this process are also poorly described in literatures.

In the present paper, the kinetics of dehydrochlorination of DCP and the hydrolysis of

EPCH have been studied, both in the presence of caustic soda.

EXPERIMENTAL

Equipment, Reagents and Operating Conditions

Both the kinetics of dehydrolorination and hydrolysis reactions was studied in presence of caustic soda. Dehydrochlorination of DCP in aqueous basic solution is a fast reaction occurring with the elimination of hydrogen chloride. In a dilute caustic soda solution, the reaction rate has been determined by using a glass complex electrode to measure the decrease of conductivity of the solution with time according to the method described by Jin *et al.* (2005). The conductivity varies with concentration of ions in the dilute electrolyte solution, and was recorded by the conductivity recorder with the measure accuracy of 0.01 mS cm^{-1} and the response time of 0.01 s, which make sure that the conductivity measurement system has high control accuracy. The temperature control device shown in Figure 1 makes sure of the temperature-control with the measure accuracy of 0.01 K.

The dehydrochlorination reaction took place in a thermo stated stirred batch reactor. Fifty millilitres of basic solution containing about 0.01 mol L^{-1} of NaOH was put into the reactor. When the reaction temperature was reached, 0.25 ml of the organic reagent was injected into the solution using a glass syringe, and the potentiometric response was recorded. Runs made with the two pure dichloropropanols isomers (1,3-DCP and 2,3-DCP) have shown identical reactivity. The kinetic data collected in this paper refer to an industrial mixture of the two isomers mentioned. The main component of these mixtures is 1,3-DCP, with little 2,3-DCP only (Krafft *et al.*, 2005).

Hydrolysis reaction was studied in a different procedure. The reactor for hydrolysis reaction study is almost the same as the reactor shown in Figure 1 but with different dimensions: diameter of 100 mm, height of 100 mm, and the diameter of the anchor-like agitator is 45 mm. The temperature control device is also the same as the one used in dehydrochlorination reaction study. Since this is a very slow reaction, the reaction rate was determined by using titration to measure the decrease of the hydroxyl ion concentration as a consequence of the reaction, and the reaction took place in a thermo stated stirred batch reactor. Three hundred millilitres of basic solution containing about 0.2 mol L^{-1} of NaOH was put into the reactor. When the reaction temperature was reached, one equivalent of EPCH per equivalent of base was used. Runs were made in the temperature range of 322.85 K–344.25 K and in the rotation rate range of 270–410 r min^{-1}.

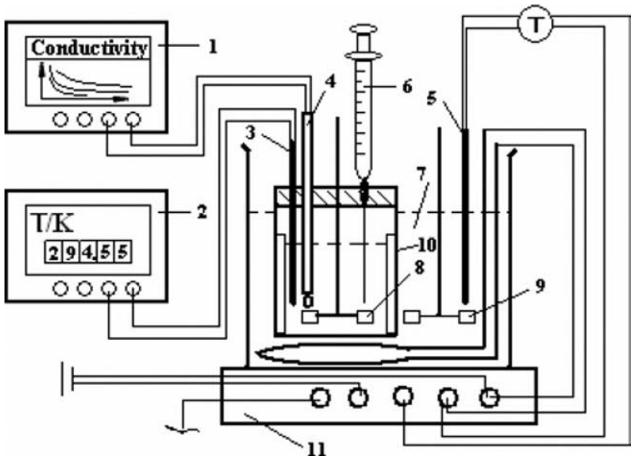

Figure 1. Conductivity measurement device: (1) conductivity recorder; (2) temperature recorder; (3) thermocouple in the reactor near the wall; (4) glass complex electrode; (5) thermocouple for the tin bath; (6) glass syringe; (7) oil; (8) anchor-like agitator with the diameter of 20 mm; (9) agitator to churn up the oil; (10) cylinder reactor with the diameter of 50 mm, the height of 50 mm and four baffles to strengthen the mixing effect; (11) temperature control device.

RESULTS

Dehydrochlorination Reaction

In the dehydrochlorination reaction, the hydroxyl ion concentration decreases rapidly during the reaction, and caused the conductivity decrease rapidly, which was recorded by the conductivity recorder. The experimental results, in fact, can be well represented by assuming a second order kinetic model, of the type:

$$r_1 = k_1[OH^-][DCP] \tag{4}$$

The whole data processing was taken according to the method mentioned by Li (2004).

Let

$$M = \frac{1}{(b-a)} \times \ln\left\{\frac{1}{\kappa_t - \kappa_\infty} \times \left[(\kappa_0 - \kappa_\infty) - (\kappa_0 - \kappa_t) \times \frac{a}{b}\right]\right\} \tag{5}$$

The experimental data were obtained for runs made in different operating conditions and the kinetic constants have been calculated on the basis of the second order kinetic model.

Figure 2 shows the values of *M* versus time for the dehydrochlorination reactions made at different temperatures. The linearity of the curves justifies the assumption of the second order for dehydrochlorination reaction, and we determined the constant *k* by the slope of the straight line.

Figure 3 shows the exponential-like variation of the kinetic constant with the temperature, compared with Figures 7–12 in literature (Hu, 1999), we can conclude that the dehydrochlorination reaction obeys the general reaction kinetics.

In Figure 4, an Arrhenius plot for this reaction is also reported. From Figure 4, one can compare the kinetic constants of the reaction in different temperature range: 293 K $\sim$ 313 K and 313 K $\sim$ 333 K. According to the Arrhenius equation (Laidler, 1987a; Kooij, 1893)

$$k = Ae^{-Ea/RT} \tag{6}$$

One can calculate the values of *Ea* and *A* for each temperature range, respectively. We can then conclude that the dehydrochlorination reaction rate in the presence of caustic soda in different temperature ranges can be expressed as:

293 K $\sim$ 313 K:

$$r_1 = 1.77 \times 10^7 e^{-41{,}000/RT}[DCP][OH^-] \tag{7}$$