

Synthesis of Epichlorohydrin from Glycerol. Hydrochlorination of Glycerol

Georgy Dmitriev S. *, Leonid Zanaevskiy N.

Federation State Unitary Organization "Karpov Institute of Physical Chemistry"
Russia, Moscow, Minusinskaya str., 11 - 311. jorik17@mail.ru

In the present study the investigation of the glycerol hydrochlorination process has been presented. It involves the steps of esterification and hydrochlorination. The kinetic parameters of the reactions have been determined. It is also shown that the water concentration increase in the reaction mixture results in the reduction of hydrochlorination rates. It has been explained by the phenomenon of solvation. The solvation effect is entered into the kinetic equation.

Introduction

At present the setting up of production facilities for the production of valuable chemicals from the renewable feedstock is one of the most important trends in the development of chemical industry. Synthesis of biodiesel from the vegetable oil is one of these trends, with glycerol being the by-product of this process (10% from the amount of produced biodiesel).

At the beginning of XXI century the rapid development of the biodiesel production in the first years resulted in oversupply of cheap glycerol into the market. Therefore the use of glycerol for the production of valuable chemicals (Pagliaro, 2008) has become economically feasible. The synthesis of epichlorohydrin (EPCH) from glycerol (GI) has been one of these routes.

The production of EPCH based on propylene has been practiced since 1947. It suffers from some undesirable features, such as raw dependence on the oil, low selectivity of reactions and consequently significant amount of toxic organic withdrawal (up to 0.5 t/t EPCH) and large amount of polluted sewage (up to 54 m³/t EPCH).

These factors prompted the search for alternative solutions that are more environment-friendly. In the first step, GI is hydrochlorinated to the mixture of 1,3-dichlorohydrin (α,γ -DCH) and 1,2-dichlorohydrin (α,β -DCH). In the second step, the mixture of dichlorohydrins is dehydrochlorinated to EPCH.

The influence of water on the reaction rate is one of the main problems at the hydrochlorination step that has been recently examined by us. The determination of the reaction kinetics, finding reasons for the reaction rate reduction with the water concentration increase and the evaluation of quantitative relationship of the above phenomenon with the kinetics have been the target of our investigation.

Equipment, analyses and operating conditions

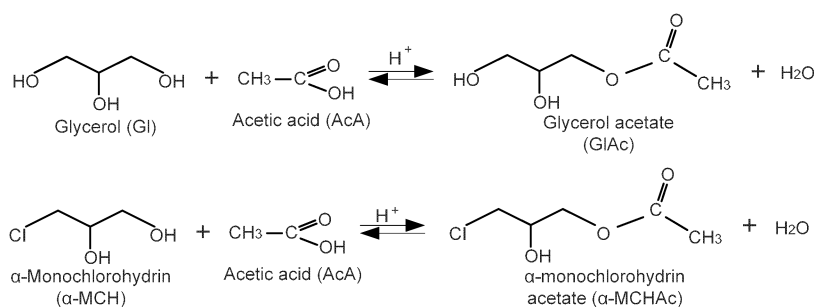
The investigation of esterification between glycerol and acetic acid was studied in batch mode in a glass reactor. It had 50 ml volume and it was equipped with a stirrer, an electric heater, a reflux condenser and a tap for output samples. Glycerol (monochlorohydrin) saturated with hydrogen chloride up to 0.7% by weight was heated up to required temperature (in the range of 59 – 98°C). Then acetic acid was injected into the reactor. The samples of reaction mixture were outputted from time to time during one run.

The investigation of hydrochlorination was studied in the wide range of water concentration (from 1.5 to 13 mol/l) in continuous mode in a glass reactor. The volume of reactor was 30 ml. It was equipped with a stirrer, an electric heater and a reflux condenser. The reaction products were removed continuously.

Joint determination of hydrochloric acid and acetic acid was carried out with the help of conductivity measurement device. Organic compounds were analyzed by gas chromatograph.

Esterification

The hydrochlorination of glycerol is catalyzed by carboxylic acids, for example, acetic acid. In this case there are esters among the reaction products. It means that there are reactions of esterification in the reaction mixture. It can be represented according to the scheme:



The modal concentration dependences on time were obtained in the experiments on these reactions study. The reaction rates are supposed to be described by the following equations (Lebedev, 1988):

- for the esterification of glycerol:

$$r_1 = k_1 \cdot C_{HCl} \cdot (C_{Gl} \cdot C_{AcA} - \frac{C_{GIac} \cdot C_{H2O}}{K_{eq1}}) \quad (1)$$

- for the esterification of α -monochlorohydrin:

$$r_2 = k_2 \cdot C_{HCl} \cdot (C_{\alpha\text{-MCH}} \cdot C_{AcA} - \frac{C_{\alpha\text{-MCHAc}} \cdot C_{H2O}}{K_{eq2}}) \quad (2)$$

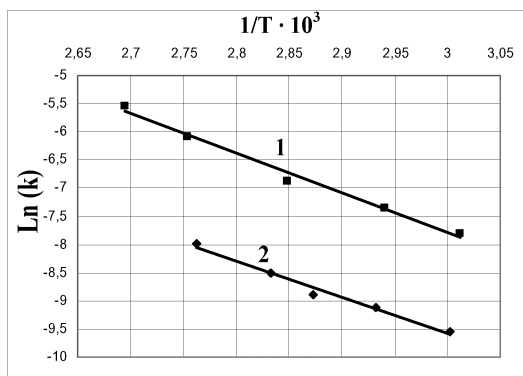


Figure 1. The Arrhenius plot for the reactions: 1 – esterification of glycerol; 2 – esterification of α -monochlorohydrin.

Using these equations the kinetic constants k_1 and k_2 were calculated with the accuracy more than 96%. The Arrhenius plot is presented in Figure 1. The analysis of experimental data allowed to calculate values of the constants:

- for the glycerol esterification:

$$k_1 = 6.29 \cdot 10^5 \cdot e^{\left(\frac{-(58500 \pm 3000)}{RT}\right)}, \text{ [l}^2 \cdot \text{s}^2 / \text{mol}^2 \text{]} \quad (3)$$

$$K_{\text{eq}1} = 1,89 \quad (4)$$

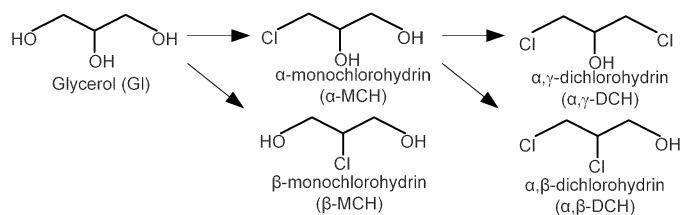
- for the α -MCH esterification:

$$k_2 = 1.60 \cdot 10^4 \cdot e^{\left(\frac{-(53000 \pm 3000)}{RT}\right)}, \text{ [l}^2 \cdot \text{s}^2 / \text{mol}^2 \text{]} \quad (5)$$

$$K_{\text{eq}2} = 1,00 \quad (6)$$

Hydrochlorination

Hydrochlorination of glycerol is described by the following scheme:



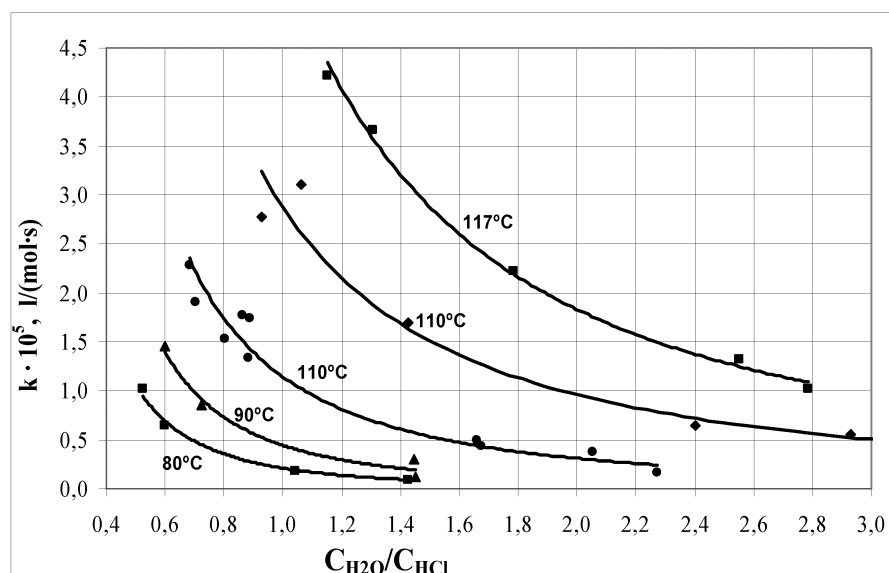


Figure 2. Dependence of kinetic constant on the molar ratio between water and hydrogen chloride for the reaction of α -MCH formation. Temperatures: 1 - 117°C; 2 - 110°C; 3 - 100°C; 4 - 90°C; 5 - 80°C.

These reactions being ones of bimolecular nucleophilic substitution S_N2 (Lebedev, 1988). Preliminary thermodynamic analysis showed that these reactions are irreversible. Therefore the hydrochlorination of glycerol is to be described by the following equation:

$$r = k \cdot C_{Gl} \cdot C_{HCl} \quad (7)$$

But implementation of this equation resulted in some unexpected data presented in Figure 2.

The obtained results showed that the kinetic constant reduces with the increase of the molar ration between water and hydrogen chloride (C_{H_2O}/C_{HCl}). The observed facts may be explained by the phenomenon of solvation (Reichardt, 1990).

There are polar organic compounds in the reaction medium such as glycerol, monochlorohydrins, dichlorohydrins. They may orientationally interact and also form hydrogen bonds both with each other and with molecules of water. But on the other hand there are chlorine anions in the same mixture. They have small radius in comparison with organic compounds and they bring negative charges. The molecules of water may solvate both glycerol (chlorohydrins) and chlorine anions. But it is clear that the latter are solvated the most strongly. When the molecules of water interact with such solvated chlorine anions it is necessary to overcome supplementary energy barrier in order to destroy solvation sphere. The more molecules of water solvate one chlorine anion the bigger energy barrier is and the less kinetic constant is.

One may say that chlorine anions solvated with one, two, three or more molecules of water are presented as different chemical compounds. Each of them has its own kinetic constant in equation (7). Data presented in Figure 2 show the dependence of the kinetic constant on the reacting compound type.

Mathematical treatment of experimental data allowed to determine equations which describe reaction rates of formation of α -MCH (8) and β -MCH (9) from ratio C_{H_2O}/C_{HCl} :

$$r_3 = 2.1 \cdot 10^9 \cdot e^{\left(\frac{-(102000 \pm 3000)}{RT}\right)} \cdot \left(\frac{C_{HCl}}{C_{H_2O}}\right)^{(10.5 - 0.023 \cdot T)} \cdot C_{Gl} \cdot C_{HCl} \quad (8)$$

$$r_4 = 2.2 \cdot 10^{12} \cdot e^{\left(\frac{-(132000 \pm 4000)}{RT}\right)} \cdot \left(\frac{C_{HCl}}{C_{H_2O}}\right)^{(14.7 - 0.034 \cdot T)} \cdot C_{Gl} \cdot C_{HCl} \quad (9)$$

The investigation of hydrochlorination of glycerol in the presence of acetic acid resulted in analogous dependences. The rate of catalytic reaction was calculated as the difference between the observed rate and the non-catalytic rate. It was determined that catalytic reactions of α -MCH (10) and β -MCH (11) formations are described by the following equations:

$$r_5 = 1.24 \cdot 10^{11} \cdot e^{\left(\frac{-(86000 \pm 1000)}{RT}\right)} \cdot \left(\frac{C_{HCl}}{C_{H_2O}}\right)^{(25.63 - 0.056 \cdot T)} \cdot C_{Gl} \cdot C_{HCl} \cdot C_{AcA} \quad (10)$$

$$r_6 = 1.38 \cdot 10^{10} \cdot e^{\left(\frac{-(91500 \pm 1000)}{RT}\right)} \cdot \left(\frac{C_{HCl}}{C_{H_2O}}\right)^{(13.36 - 0.026 \cdot T)} \cdot C_{Gl} \cdot C_{HCl} \cdot C_{AcA} \quad (11)$$

Also it was obtained that the non-catalytic rate was less than 3% of the observed rate. That is why the investigation of α, γ -DCH and α, β -DCH formation reactions were studied only in the presence of acetic acid. The following equations were obtained for α, γ -DCH (12) and α, β -DCH (13):

$$r_7 = 2.51 \cdot 10^4 \cdot e^{\left(\frac{-(47000 \pm 1000)}{RT}\right)} \cdot \left(\frac{C_{HCl}}{C_{H_2O}}\right)^{(35.74 - 0.084 \cdot T)} \cdot C_{\alpha-MCH} \cdot C_{HCl} \cdot C_{AcA} \quad (12)$$

$$r_8 = 1.62 \cdot 10^8 \cdot e^{\left(\frac{-(92000 \pm 1000)}{RT}\right)} \cdot \left(\frac{C_{HCl}}{C_{H_2O}}\right)^{(16.85 - 0.038 \cdot T)} \cdot C_{\alpha-MCH} \cdot C_{HCl} \cdot C_{AcA} \quad (13)$$

Conclusion

The reactions of esterification of glycerol and α -MCH, catalytic and non-catalytic formations of α -MCH and β -MCH, catalytic formations α,γ -DCH and α,β -DCH have been studied. The kinetic equations of these reactions were determined.

The obtained data prove that the esterification proceeds quickly and glycerol (chlorohydrin) is always in the equilibrium with its acetate. Hydrochlorination of glycerol (monochlorohydrin) is irreversible and proceeds more slowly. The feature of hydrochlorination reactions are the reduction of reaction rate with the increase of ratio C_{H_2O}/C_{HCl} . The solvation of chlorine anion is considered to be the cause of this phenomenon. Therefore it is reasonable to remove water from the reaction mixture.

Nomenclature

AcA – acetic acid

EPCH - epichlorohydrin

Gl – glycerol

GIAc – glycerol acetate

α,β -DCH – α,β -dichlorohydrin

α,γ -DCH – α,γ -dichlorohydrin

α -MCH – α -monochlorohydrin

β -MCH – β -monochlorohydrin

C_{AcA} – concentration of acetic acid, mol/l

C_{Gl} – concentration of glycerol, mol/l

C_{GIAc} – concentration of glycerol acetate, mol/l

C_{HCl} – concentration of hydrogen chloride, mol/l

C_{H_2O} – concentration of water, mol/l

$C_{\alpha-MCH}$ – concentration of α -monochlorohydrin, mol/l

$C_{\alpha-MCHAc}$ – concentration of α -monochlorohydrin acetate, mol/l

r – reaction rate, mol/(l·s)

k – kinetic constant

K_{eq} – equilibrium constant

References

- Lebedev N.N., 1988, Chemistry and technology of basic organic and petrochemical synthesis. Chemistry, Moscow, Russia (in Russian).
- Pagliari M, Rossi. M., 2008, The future of glycerol. New usages for a versatile raw material. RSCPublishing, Cambridge, UK.
- Reichardt C., 1990, Solvents and solvent effects in organic chemistry. VCH, Weinheim, Germany.