# Kinetic Modeling of Ethylene Glycol Monoesterification

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ABSTRACT: The monoesterification of ethylene glycol under isothermal conditions was conducted using benzoic acid in methane-sulfonic acid/Al<sub>2</sub>O<sub>3</sub> as a catalyst. Using this reagent, glycol was selectively monoesterified with high yield. The reactions were performed within an automated batch reactor under equimolar conditions, constant rotational frequency of the stirrer, and within the temperature range from 65 to 85°C. The rate constant related to this reaction and to the corresponding reverse reaction, activation energy, and preexponential factor was derived from experimental data. It has been concluded that under these conditions the formation of dibenzoate was successfully prevented. © 2015 Wiley Periodicals, Inc. Int J Chem Kinet 47: 658–663, 2015

# INTRODUCTION

Esters are industrially very important products. Esters of different alcohols and acids are used as pharmaceuticals and pharmaceutical intermediates, flavors, lubricants, emulsifiers, and additives applicable within the food, beverages, cosmetics, and utility chemicals industries [1]. They can be synthesized by esterification of carboxylic acids, transesterifications of methyl or ethyl esters, or alkylation of carboxylic anions [2]. The applications of solid catalysts for the esterification and/or transesterification of carboxylic acids or esters with alcohols compared to homogeneous catalysts (mineral acids, metal hydroxide, and metal alkoxide) are preferable. Heterogeneous catalysts are much easily separated from the reaction mixture, and the purity of the products is higher because side reactions can be completely eliminated or are less significant; it is possible to work under milder and solvent-free reaction conditions and also what is of great importance we can develop safer and nonwaste producing reactions [2–5]. Nevertheless, there are economic demands toward the uses of solid catalysts instead of the liquid ones. For the replacement of those corrosive liquid acids that are currently used, solid acid catalysts such as zeolites, clays, sulfated metal oxides, heteropolyacids, ion-exchange resins can be applied [6,7].

Esterification reactions are reversible equilibriumlimited reactions in which water is produced as a byproduct. Water effects the conversion and activity of an acidic catalyst. Therefore, in some cases water is removed from the reaction mixture to improve the efficiency of the reaction [8,9]. The downside of such reactions is also the poor selectivity leading to undesirable side reactions and low yields. These weaknesses can be overcome by the application of specific catalysts [5,6].

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Figure 1 Reaction scheme for the monoesterification and diesterification of ethylene glycol with benzoic acid.

The synthesis of esters attracts the attention of many researchers because of its widespread application. Despite of the disadvantages of using homogeneous acid catalyst, the kinetic studies of homogeneous esterifications are still very important [10–12]. But there is an increasing tendency toward development of a process that meets the requirements of safety and minimum waste. Cation exchange resins are there for a reasonable choice of solid catalysts [13–15].

The presented paper reports on a kinetic study of ethylene glycol monoesterification with benzoic acid that was carried out in  $Al_2O_3/MeSO_3H$  as a catalyst. This catalyst was chosen because it is very effective, it has high selectivity toward the monoester, and it is inexpensive [2]. Various parameters were determined such as equilibrium reaction rate constants, activation energies, and preexponential factors. A considerable amount of published work is available on the esterification systems, but none of these studies considered the kinetics of the mentioned esterification using a specified catalyst.

#### EXPERIMENTAL

#### Materials

All the chemicals, ethylene glycol ( $w \ge 99.0\%$ ; Fluka, Belgium), benzoic acid ( $w \ge 99\%$ ; Merck, Hohenbrunn, Germany), methane-sulfonic acid (anhydrous; Aldrich, France), aluminum oxide (anhydrous; Merck, Darmstadt, Germany), calcium chloride ( $w \ge 97.0\%$ ; Sigma-Aldrich, China), sodium hydrogen carbonate ( $w \ge 99.0\%$ ; J.T. Baker, Deventer, Holland), and chloroform (w = 99.0-99.4%; Merck, Darmstadt, Germany) are commercially available and were used as received without further purification.

#### Equipment

An automated, computer in-line controlled and regulated reaction calorimeter (Mettler Toledo RC1e, Greifensee, Switzerland) was used to conduct the experimental work. The 0.8-L double-walled glass-made laboratory batch reactor was equipped with a propeller glass stirrer, a glass AP01 temperature sensor, and the FTIR-based ReactIR<sup>TM</sup> iC10 analysis system coupled with a flexible Silver Halide (AgX) FiberConduit<sup>TM</sup>, and 6.3 mm DiComp<sup>TM</sup> probe, which was used for the real-time monitoring of 2-hydroxyethyl benzoate concentration profiles.

# **Experimental Procedure**

Monoesterification of ethylene glycol under isothermal conditions was conducted using benzoic acid in  $Al_2O_3/MeSO_3H$  as a catalyst. The reaction scheme in Fig. 1 shows two reversible competitive esterification reactions, which led first to monoester and further to diester. The purpose of our work was to maximize the yield of monoester. The synthesis procedure was proven to be very effective and highly selective for monoesterification and was reported by Sharghi and Sarvari [2]. The selectivity toward the formation of monoester was also increased by using equimolar amounts of ethylene glycol and benzoic acid.

All the experiments were carried out within a RC1e reactor system (Mettler Toledo) at a rotational

frequency of the stirrer  $f_{\rm m} = 250 \text{ min}^{-1}$ , and reaction media temperatures  $\vartheta = 65, 70, 75, 80, \text{ and } 85^{\circ}\text{C}.$ The individual experiment was started by charging the RC1e reactor with methane-sulfonic acid (m =250 g) and benzoic acid (m = 20.63 g). The medium was stirred at the defined rotational frequencies of the stirrer and heated up to the desired reaction medium temperature. Thereupon, Al<sub>2</sub>O<sub>3</sub> was slowly charged to the reaction medium (m = 45.61 g). The monoesterification was triggered by the addition of ethylene glycol (m = 10.49 g), and the progress of the reaction was monitored using the FTIR-based ReactIR<sup>TM</sup> iC10 analysis system. The ReactIR iC software was used to control the spectrometer and to collect the spectra every 2 min. All the spectra collected during the experiments were measured against a background spectrum of air.

#### **Analytical Procedure**

2-Hydroxyethyl benzoate is not commercially available, thus for real-time monitoring the end product of monoesterification was further cleaned to remove the catalyst and nonreactive reagents as described by Sharghi and Sarvari [2]. The reaction mixture was cooled and poured into distilled water. The mixture was twice extracted with chloroform. Both phases were separated. The organic phase was washed with a saturated solution of sodium hydrogen carbonate and dried over calcium chloride. After the filtration, the chloroform was evaporated under reduced pressure, p =40 mbar, and temperature,  $\vartheta = 50^{\circ}$ C. The residue (pure 2-hydroxyethyl benzoate) was used to prepare standard solutions. FTIR-ATR spectra of ethylene glycol (a), benzoic acid (b), and 2-hydroxyethyl benzoate (c) were collected on a Shimadzu IRAffinity-1 spectrophotometer (Fig. 2).

For comparing the spectra of ethylene glycol, dibenzoate was gathered from the Spectral Database for Organic Compounds, which was compiled by the National Institute of Advanced Industrial Science and Technology, Japan. The main difference among monoester and diester spectra is in the lack of a broad peak in the diester spectra that corresponds to O–H group stretching within the range of wave numbers  $3200-3550 \text{ cm}^{-1}$ .

For the preparation of the calibration curve (Fig. 3), 2-hydroxyethyl benzoate was diluted in methanesulfonic acid to obtain solutions with concentrations, w = 0, 2, 4, 6, 8, 10, 12, and 14%.

The real-time concentration profiles of 2hydroxyethyl benzoate during the reaction were obtained by calculating the areas (S) of two point



**Figure 2** FTIR–ATR spectra of ethylene glycol, benzoic acid, and 2-hydroxyethyl benzoate (*y* axis represents transmittance 5–100%.



Figure 3 Calibration curve for 2-hydroxyethyl benzoate in methane-sulfonic acid.

baseline of the corresponding peak within the wave number range,  $v = 1440-1470 \text{ cm}^{-1}$ .

#### **Kinetic Model**

For the bimolecular-type second-order reaction,

$$A + B \leftrightarrow R + S$$

with the restrictions that  $c_{A0} = c_{B0}$  and  $c_{R0} = c_{S0} = 0$ and the equilibrium constant must be

$$K = \frac{k_1}{k_2} = \frac{c_{\rm R} c_{\rm S}}{c_{\rm A} c_{\rm B}} \tag{1}$$



Figure 4 Waterfall plot of FTIR spectra during the monoesterification of ethylene glycol at a temperature,  $\theta = 70^{\circ}$ C.

the integrated rate equation is as follows:

$$\ln \frac{X_{Ae} - (2 X_{Ae} - 1) X_A}{X_{Ae} - X_A} = 2 k_1 \left(\frac{1}{X_{Ae}} - 1\right) c_{A_0} t$$
(2)

where  $c_{A0}$  is the initial concentration of ethylene glycol or benzoic acid,  $k_1$  the reaction rate constant for the forward reaction,  $X_A$  conversion,  $X_{Ae}$  equilibrium conversion, and *t* time.

The adequacy of this kinetics can be tested using the plot of Eq. (1) and fitting this equation within the experimental data.

The average absolute deviation (AAD) between experimental and calculated values was obtained as follows:

AAD (%) = 
$$\frac{100}{N} \sum_{i=0}^{N} \left( \frac{X_{A \operatorname{cal} i} - X_{A \exp i}}{X_{A \exp i}} \right)$$
 (3)

where,  $X_{A \operatorname{cal} i}$  is calculated conversion,  $X_{A \exp i}$  is experimental conversion, and *N* is the number of experimental points.

#### **RESULTS AND DISCUSSION**

The FTIR-based analysis system was used for the realtime monitoring of 2-hydroxyethyl benzoate concentration profiles within an automated laboratory batch reactor. As an example, the FTIR spectra collected during one selected experiment is presented in Fig. 4.

It can be clearly seen that the intensity of the peak (absorbance, A) within the wave number range,  $\nu = 1440-1470 \text{ cm}^{-1}$ , increases over the reaction time. After a certain period of time, depending on the experimental conditions, equilibrium steady state is formed.

As already mentioned, we wanted to maximize the production of 2-hydroxyethyl benzoate and that was achieved by conducting the reaction under equimolar conditions and with the selection of a specific catalyst Al<sub>2</sub>O<sub>3</sub>/MeSO<sub>3</sub>H. For this catalyst, the high 94% yield toward monoester was already reported by Sharghi and Sarvari [2]. Thus, all the assumptions regarding the experimental procedure were confirmed by gathering the FTIR spectra of our end product.

After analytical integration of the rate expression for second-order reversible reaction, the performance equation was developed. By plotting the term  $\ln(X_{Ae} - (2X_{Ae} - 1)X_A)/(X_{Ae} - X_A)$  versus time, it was possible to calculate the reaction rate constant,  $k_1$ . Another constant,  $k_2$ , for the reverse reaction was obtained from the equilibrium constant equation (2). Experiments at five different temperatures were studied. Each single experiment was conducted at least twice.

From the Arrhenius plot (Fig. 5), we determined the activation energy and the preexponential factor for the forward reaction and for the reverse reaction, respectively. The obtained values of main kinetic parameters are listed in Table I.



**Figure 5** Experimental and Arrhenius model–based values of the logarithm of reaction rate constants,  $\ln k_1$  and  $\ln k_2$ , in relation to 1/T.

**Table I**Activation Energies and PreexponentialFactors for Forward and Reverse Reactions

Variable	Forward Reaction	Reverse Reaction
$\overline{E_a \text{ (kJ mol}^{-1})}$ $k_0 \text{ (L mol}^{-1} \text{ min}^{-1}\text{)}$	$100.4 \pm 1.8$ $(3.6 \pm 3.1) \times 10^{12}$	$\begin{array}{c} 118.3 \pm 1.8 \\ (1.1 \pm 1.0) \times 10^{14} \end{array}$

The comparison of experimental and calculated values of the conversion for one selected experiment is presented in Fig. 6.

As it can be seen from Fig. 6, the comparison between experimental and calculated values of the conversion is satisfactory. The average absolute deviation for the 1844 experimental data was 4.7%.

The selected reaction was chosen for the kinetic study because the synthesis of glycol monoesters of diols has a widespread applications particularly



Figure 6 Experimental and calculated values of conversion in relation to time at a temperature,  $\vartheta = 65^{\circ}$ C.

in pharmaceutical industry. Using a mixture of  $Al_2O_3/MeSO_3H$  as a catalyst effectively prevents the concurrent formation of diesters, forcing into a tedious separation procedure. In spite of considerable amount of published work on monoesterifications, kinetics of the reaction involved has not been studied. Since the reaction rate also depends on the type of catalyst, the complete study was performed for monoesterification of ethylene glycol with benzoic acid using  $Al_2O_3/MeSO_3H$  as a highly selective ability reagent. Consequently, the comparison of obtained kinetic parameters was impossible because for the selected reaction and used catalyst; no literature data were found.

#### CONCLUSION

The literature contains numerous reports on kinetic models of consecutive chemical reactions. However, much less attention has been paid to the design for the equally prevalent class of reversible reactions.

The forward and reverse reaction rate constants, activation energies, and preexponential factors of the reversible monoesterification of ethylene glycol with benzoic acid catalyzed by  $Al_2O_3/MeSO_3H$  were estimated from the experimental data. It has been indicated that the reaction can be interpreted using the second-order reversible reaction kinetic model. By providing equimolar conditions and by the use of a specific catalyst, we effectively produced a monoester. As the synthesis of glycol monoesters of diol has received considerable interest in view of their widespread applications, prevention of concurrent forming of diesters is notable.

The results of this study could be applied to the control of investigated chemical reactions at the molecular level, which strongly depends on kinetics and mechanism.

#### NOMENCLATURE

- A Absorbance
- $c_{A0}$  Initial concentration of ethylene glycol or benzoic acid, mol L-1
- $E_{\rm a}$  Activation energy, kJ mol-1
- $f_{\rm m}$  Rotational frequency of the stirrer, min-1
- k Reaction rate constant,  $L \mod{-1} \min{-1}$
- $k_0$  Preexponential factor in Arrhenius equation, L mol-1 min-1
- m Mass, g
- N Number of experimental points
- S Surface area
- t Time, s
- T Temperature, K

- v Wave number, cm-1
- V Volume of reaction mixture, L
- *w* Mass concentration, %
- *X*<sub>A</sub> Conversion
- X<sub>Ae</sub> Equilibrium conversion

### **GREEK SYMBOL**

*θ* Temperature, °C

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