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Effect of water on sulfuric acid catalyzed esterification

Yijun Liu, Edgar Lotero, James G. Goodwin Jr. *

Department of Chemical and Biomolecular Engineering, Clemson University, Clemson, SC 29634, USA

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Abstract

This paper reports on an investigation into the impact of water on liquid-phase sulfuric acid catalyzed esterification of acetic acid with methanol at 60 °C. In order to diminish the effect of water on the catalysis as a result of the reverse reaction, initial reaction kinetics were measured using a low concentration of sulfuric acid (1×10^{-3} M) and different initial water concentrations. It was found that the catalytic activity of sulfuric acid was strongly inhibited by water. The catalysts lost up to 90% activity as the amount of water present increased. The order of water effect on reaction rate was determined to be -0.83. The deactivating effect of water also manifested itself by changes in the activation energy and the pre-exponential kinetic factor. The decreased activity of the catalytic protons is suggested to be caused by preferential solvation of them by water over methanol. A proposed model successfully predicts esterification rate as reaction progresses. The results indicate that, as esterification progresses and byproduct water is produced, deactivation of the sulfuric acid catalyst occurs. Autocatalysis, however, was found to be hardly impacted by the presence of water, probably due to compensation effects of water on the catalytic activity of acetic acid, a weak acid.

Keywords: Esterification; Acid catalysis; Water effect; Proton solvation; Sulfuric acid

1. Introduction

Esterification of carboxylic acids with alcohols represents a well-known category of liquid-phase reactions of considerable industrial interest due to the enormous practical importance of organic ester products. These ester products include environmentally friendly solvents, flavors, pharmaceuticals, plasticizers, polymerization monomers and emulsifiers in the food, cosmetic and chemical industries [1–3]. Recently, a growing interest in ester synthesis has been further stimulated due to the great promise shown by long chain mono alkyl esters as fuels for diesel engines [4,5].

Esterification can take place without adding catalysts due to the weak acidity of carboxylic acids themselves. But the reaction is extremely slow and requires several days to reach equilibrium at typical reaction conditions. Either homogenous mineral acids, such as H_2SO_4, HCl or HI, or heterogeneous solid acids, such as various sulfonic resins, have been shown to be able to effectively catalyze the reaction. The catalysts essentially promote the protonation of the carbonyl oxygen on the carboxylic group, thereby activating nucleophilic attack by an alcohol to form a tetrahedral intermediate [5]. Disproportionation of this intermediate complex ultimately yields the ester (refer to Fig. 1).

In spite of the long history of esterification and the large amount of literature concerning the performances of various catalysts and the kinetics of different ester syntheses, there are still many fundamental issues that remain poorly understood. For instance, an important subject that needs to be better understood is the effect that water produced from esterification may have on the acid catalysis. Pronounced inhibition effects of water on homogenous acid catalyzed esterification have been reported by different researchers [4,6–8]. For example, Aafaqi et al. [4] showed that, when esterification was carried out using homogenous *para*-toluene sulfonic acid (*p*-TSA) with an initial 15 vol% water, the conversion of carboxylic acids was decreased by around 40% (after 4 h of reaction). Similarly, Hu et al. [7] found that homogenous $H_3PW_{12}O_{10}$ lost about 30% of its catalytic activity when only 7.5 mol% water was introduced into the esterification of propionic acid with isobutyl alcohol at 70 °C.

Few studies, however, have ever focused on how water actually affects reaction activity. The decrease in esterification kinetics in the presence of water has generally been attributed to reverse hydrolysis [4,6]. The water retardation effect on ester formation, however, is not limited to esterification. Acid catalyzed

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* Corresponding author. Tel.: +1 864 656 6614; fax: +1 864 656 0784.
E-mail address: james.goodwin@ces.clemson.edu (J.G. Goodwin Jr.).

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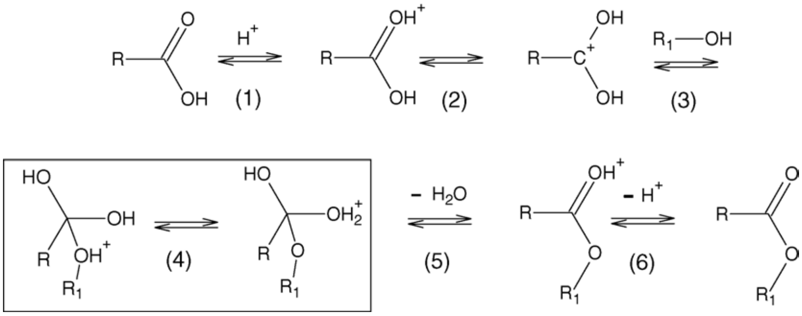

Fig. 1. Mechanistic route of acid catalyzed esterification.

transesterification has also been found to be inhibited in the presence of water [6,7,9,10]. Moreover, when carried out in an alcoholic medium, acid catalyzed hydrolysis has been found to be faster than in an aqueous medium [11,12]. Obviously, these observations suggest that the effect of water on esterification is more than just simple reverse hydrolysis. Smith [13], based on the assumption that the interaction between protonated methanol and carboxyl acid was the rate-determining step, ascribed the effect of water on esterification to the competition for protons between water and methanol. More recently, it has been suggested that the hindered catalyst performance is due to the reduced acid strength of the catalyst caused by the coordination of water to protons [7].

Currently, knowledge regarding how water affects the efficiency of acid catalysts for esterification is quite limited and mostly qualitative. Thus, the focus of the present study was to increase the quantitative and conceptual understanding of the deactivating effect of water on acid catalyzed esterification. Here, the esterification of acetic acid with methanol using sulfuric acid was investigated with different initial water concentrations.

2. Experimental

2.1. Material

Reagents including methanol (99.9%, Acros Organics), acetic acid (99.7%, Aldrich) and water (HPLC, Acros Organics) were used without further purification. Because both methanol and acetic acid are hygroscopic, the moisture contents of the reagents were determined by Galbraith Laboratory using Karl Fischer titration. The analysis showed water contents of 160 ppm for methanol and 961 ppm for acetic acid. These moisture contents were able to be ignored since they were very small compared to the amount of water produced during the initial reaction period.

2.2. Reaction procedure

Kinetic measurements were carried out in a Parr 4590 batch reactor that consisted of a stainless steel chamber of 50 ml, a three-blade impeller and a thermocouple. The temperature was maintained within ±0.5 °C. Prior to reaction, a predetermined amount of reagent mixture was loaded into the reactor and heated to the desirable temperature while being stirred at 850 rpm. This mixing speed was determined to be sufficient to eliminate any mass transfer limitations. No change in reaction rate was detected when the stirrer speed was varied from 567 to 1417 rpm. The catalyst, concentrated sulfuric acid alone or diluted in a small amount of methanol, was charged into the reactor to initiate reaction. Although esterification occurs during the heating period due to autocatalysis, this starting method of reaction was the best way to ensure good control of temperature, which is particularly important for accurate determination of initial reaction kinetics (below 10% conversion of the limiting reagent). A microscale syringe was used for sampling at definite time intervals. A sample was always taken right before catalyst charging as the zero point for every run. Samples from the reaction mixture were immediately diluted in cold 2-propanol, and reaction stopped because of cooling and dilution.

A Hewlett-Packard 6890 gas chromatograph equipped with a DB-1 column ($0.32\,\text{mm} \times 30\,\text{m} \times 0.53\,\mu\text{m}$) and a FID detector was used for sample analysis with toluene as an internal standard. The concentrations of all species (except water) were accurately quantified and found to obey well the stoichiometry of the reaction, which along with the nonappearance of unknown peaks as detected by GC analysis indicated the absence of side reactions under the experimental conditions used.

2.3. Experimental design

In order to better observe the effect of water on reaction and to minimize the contribution of reverse hydrolysis, a small amount of catalyst ($C_C = 1 \times 10^{-3}\,\text{M}$) was used and attention was focused particularly on the initial period of reaction. A series of experiments with varying amounts of initial water addition were carried out at 60 °C with a fixed catalyst concentration. Table 1 shows initial concentrations of reagents and the concentrations of water initially added. The initial water concentrations used corresponded to the amounts of water that could have been produced by esterification at different conversions. The idea behind this approach was to observe how catalyst activity is affected with increasing concentration of water, as occurs during esterification.

Because the molar ratio of methanol-to-acetic acid was kept constant and no solvent was used, kinetic comparisons are based on reaction constants instead of reaction rates. As mentioned earlier, esterification can be autocatalyzed by acetic acid itself.