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Screening of potential complexing agents in methyl formate hydrolysis

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ABSTRACT

More than 70 individual compounds, mainly amines, natural products, organophosphates and sulfur-containing organic compounds, deemed as having potentially suitable complexing strength were screened in order to determine their ability to improve the equilibrium conversion of methyl formate hydrolysis. In fact, alkylphosphates, natural products and organosulfur compounds gave lower methyl formate conversions. After careful screening and investigation of the different classes of amines, aromatic heterocyclic and some tertiary amines were chosen for further investigation. However, it was discovered that imidazoles and substituted piperazines came closest to fulfilling most of the selection criteria as a good complexing agent due to their ability to form a reversible ion pair with the acid product, in addition to their high boiling point, low nucleophilic strength, less bulkiness and thermal stability. A general procedure was proposed for the screening of potential complexing agents. This approach was proven as a rapid one, consumed fewer chemicals and could be used to estimate the complexation power of different candidate compounds in the hydrolysis–complexation process when accurate calculation tools are not available.

1. Introduction

The relatively low equilibrium conversion of industrially applied reactions such as esterification, etherification and ester hydrolysis has been a bottleneck for a long time. These processes are often slow, reversible and thus inevitably limited by chemical equilibrium. In essence, the equilibrium can be improved by increasing the concentration of one of the reactants, but this approach does come with its own limitations. An example is the hydrolysis of methyl formate (MeFo), which accounts for more than 70% of the global formic acid production process [1]. In this case, an excess amount of water is added to drive the equilibrium forward, with the associated problem of finding an energy-efficient way of removing the water [2]. Alternatively, the formic acid product can be extracted from the reaction mixture to another phase with N-formylmorpholine and subsequently distil from the solvent [3].

Another approach to process intensification is to shift the equilibrium towards the products by adding a complexing agent (X), which interacts with one of the products [4]. The reacting molecules start to feel the system as an irreversible one and consequently, higher amounts of products are formed. In effect, as the formic acid is produced from methyl formate hydrolysis, it tends to dissociate and H^+ is produced. The complexing agent, present as an initial charge, starts to capture the acid as more H^+ accumulates in the solution. The complexing agent, in fact serves a dual role: it catalyzes the reaction slightly and improves the equilibrium conversion. The reaction is a two-step process, which involves the slow, endothermic hydrolysis reaction and the fast, exothermic complexation step.

The complexing agent should not interact with the reactants but form a relatively strong reversible liquid adduct (ion pair) with the carboxylic acid. This, in turn, will enhance the easy recovery of the acid and facilitate a more straightforward recycling of the organic base — a key feature of an industrially feasible process. The choice of a suitable 'X' is vital in terms of the whole process since an 'X' with a too strong complexing power results in difficulties upon distillation, causing an extra load of product to circulate in the process. Likewise, a too weak X is incapable of shifting the equilibrium. In the absence of a complexing agent and with a water-to-MeFo initial molar ratio of 1.8, the equilibrium conversion reachable is about 0.3 mol/mol [5]. Therefore, it is expected that the complexing agent should improve the equilibrium conversion considerably.

Until today, no detailed, systematic study of the complexing ability of organic bases with regard to methyl formate hydrolysis was presented in open literature. However, a lot of research efforts have been devoted to analogous processes such as the extraction of carboxylic acids, including that of formic acid, taking advantage of amines [6–9] or phosphorus-bonded, oxygen-containing extractants [10]. For instance, Hu and Adeyiga investigated the extraction of formic acid produced from the reaction of sodium formate with carbon dioxide [11]. Furthermore, Salman and co-workers

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[12] did a calorimetric study of the reaction between formic acid and N,N,N′,N′-tetramethylethylenediamine with regard to its thermal energy storage. The major differences between the extraction and hydrolysis–complexation processes (HCP) are the absence of diluent/solvent and the presence of water as one of the reactants in HCP. The earliest work that described the hydrolysis of methyl formate in the presence of n-pentylimidazole was published as a patent [13]. Recently, our group studied the kinetics of both ethyl and methyl formate hydrolyses using butyl imidazole as the complexing agent [4].

The aim of this work is to draw attention to this approach of screening different organic bases and determining their capabilities to improve the methyl formate conversion, while using a stoichiometric amount of water. The procedure is rapid and consumes fewer chemicals. The description, nature and structure of the adduct formed between formic acid and the complexing agent are beyond the scope of this work.

2. Complexation equilibria

In the current work, the reaction system, i.e. the hydrolysis and complexation steps can be represented by the following steps,

$$HCOOCH_3(A) + H_2O(B) \overset{slow}{\rightleftharpoons} HCOOH(C) + CH_3OH(D) \quad (I)$$

$$HCOOH(C) + \alpha X \overset{rapid}{\rightleftharpoons} HCOO^- XH^+(CX) \quad (II)$$

where α is the stoichiometric coefficient, which in practice might not approach unity. The complexation step (II) is the first reaction that will occur in the presence of a base since it involves the transfer of proton. When α is less than one, it implies that more than one acid per X is formed by the complex. The equilibria of Reactions (I) and (II) respectively, if the activity coefficients are approximated to unity, can be described as

$$K_1 = \frac{C_C C_D}{C_A C_B} \quad (1)$$

$$K_2 = \frac{C_{CX}}{C_C C_X^{\alpha}}. \quad (2)$$

In the absence of X, the equilibrium conversion of the hydrolysis step, $K_1 = 0.2$ at H_2O/MeFo molar ratio of 1.8 [5]. If the total concentration of acid in the system, $C_{TOT} = C_{CX} + C_C$ and f = mole of acid bound per mole of total acid (i.e. C_{CX}/C_{TOT}), then

$$K_2 = \frac{C_{CX}}{(C_{TOT} - C_{CX})C_X^{\alpha}}, \text{ which is simplified to}$$

$$K_2 = \frac{f}{C_X^{\alpha}(1-f)} \text{ for which } f<1. \quad (3)$$

The equilibrium constant of the complex formation is a function of f, which depends on the nature of the complexing agent and the acid–X interaction, which in turn depends on the initial charge of the complexing agent. It can be deduced from Eq. (3) that K_2 approaches its maximum value when there is no free acid ($C_C \to 0$) and K_2 is small when the proportion of the formic acid that formed the complex is small. When there is no additive in the system, C_C approaches its maximum value, determined by Equilibrium (I).

It was difficult to get a reliable chemical analysis method for C, X, and CX in the hydrolysis solution and A was volatile, thus, D (methanol) was selected as the key component since it was the most reliable one during the chemical analysis. In order to estimate the complexing power of the 'X', the concept of apparent equilibrium constant, $K_{1,app}$ was introduced to describe the new value obtained for K_1 of the HCP when X was added as the initial charge into the hydrolysis solution. In the HCP, X picked up C, resulting in an increase in the yield of D as more A and B reacted in contrast to the hydrolysis process, where the yield of D is less under the same reaction conditions. The concentration of the other components was based on the analysis of the component 'D'. Therefore, the apparent equilibrium constant when activity coefficients were assumed to be unity, resulted in an expression:

$$K_{1,app} = \frac{C_C^* C_D^*}{C_A^* C_B^*} \quad (4)$$

where C* represents the new concentration due to the presence of a complexing agent in the solution. The fraction of the free formic acid in the solution may be represented as

$$f = \frac{C_C}{C_{TOT}} = \frac{K_1}{K_{1,app}}$$

where ($C_C^* = C_{TOT}$).

The equilibrium constant of the complexation step can be expressed as

$$K_2 = \frac{f}{C_X^*(1-f)(1-fq)^{\alpha}}$$

where $C_X^* = C_{CX} + C_X$ and $q = \frac{C_{TOT}}{C_X^*}$.

When $q \to 1$, $C_X^* = C_{CX} \approx C_C^*$, therefore the value of K_2 can be estimated from the experimental results:

$$K_2 = \frac{f}{C_C^*(1-f)^{\alpha+1}}.$$

3. Experimental section

3.1. Pre-screening stage

The experimental work consisted of three parts namely the pre-screening, screening and the stability tests. The purpose of the pre-screening was to set selection criteria for the actual screening stage. The pre-screening was performed in about 6.3 ml scale, air-tight isobaric mini-reactors (autoclave-type 'bomb' reactors). These reactors (Fig. 1) are made of stainless steel and can withstand high pressures and temperatures. In the preliminary study, more than 70 organic bases were tested and the pre-screening involved measuring

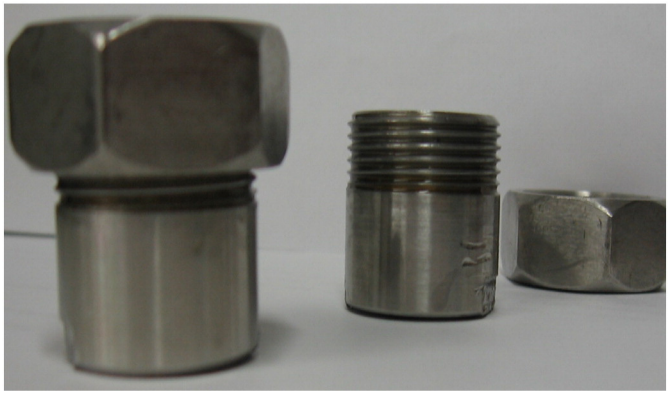

Fig. 1. Reactors used for hydrolysis–complexation process (pre-screening stage).