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Complexation equilibria studies of alkyl formate hydrolysis in the presence of 1-butylimidazole

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ABSTRACT

Formic acid production by ethyl or methyl formate hydrolysis was improved using 1-butylimidazole as a complexing agent. The chemical process involved both hydrolysis and complexation steps. The complexation equilibria were investigated by deriving theoretical equations using the equilibrium constant of the hydrolysis step, the apparent formation constant of the complexation process and the initial concentration of the complexing agent. The treatment of the experimental results within the experimental domain indicated that an equimolar amount of the acid and the base did not lead to the complex formation. Experimental observation suggested that the derived equation could be simplified by assuming that the stoichiometric coefficient of the complexing agent was 0.5. The apparent reaction enthalpy obtained from this equation was compared to the experimental one using a Tian-Calvet calorimeter and a good agreement was found between them. FTIR spectroscopy was used to confirm the existence of the complex between formic acid and 1-butylimidazole.

1. Introduction

Alkyl formate hydrolysis is a weakly endothermic reaction ($\Delta H_R^o = +16$ kJ/mol) limited by equilibrium ($K_C \leq 0.2$ at 80–110 °C, when the water-to-ester ratio is 1.8) [1,2]. The product of the reaction is formic acid and its parent alcohol. The rate of the reaction is slow but can be enhanced by both acidic and basic catalysts. In the absence of any catalyst, the reaction is self-catalyzed (autocatalysis). This implies that the formic acid ($pK_a = 3.75$) [3] formed catalyzes its own reaction . Furthermore, the organic acid can be added at the beginning of the reaction to catalyze the reaction as an initial charge. In this way, no catalyst separation is required in the process. This process has been developed into a commercial venture by various firms as far back as 1970s [4] and a lot of research efforts are undergoing to overcome the unfavourable equilibrium position of the reaction. One of the approaches is to use an organic base to reversibly complex the component of interest (acid product) [5] and then regenerate the base by distillation. 1-Butylimidazole has been reported to improve the equilibrium conversion by more than 100% through complexation of formic acid formed in the first step, i.e. hydrolysis of alkyl formate [1,2]. 1-Butylimidazole has a significant effect concerning the hydrolysis step (enhanced reaction rate and better equilibrium conversion). Alkylimidazoles, $N(CH_2)_2NRCH_2$ are stable aromatic bases, which contains one pyrrole-like and one pyridine-like N-atom at positions 1 and 3 respectively [6]. The pyrrole-like N-atom contributes two electrons to the π-electronic sextet and is therefore not basic. The non-bonding electron pair is localized onto the pyridine-like N-atom which renders imidazole nucleophilic. The structure of 1-alkylimidazole is depicted in Scheme 1. 1-alkylimidazoles are moderately strong organic bases, characterized by their high boiling points and good stability to oxidizing and reducing agents [7]. These attributes make them ideal candidates for complexing agents. The basic site is the N-3 and many imidazolium derivatives coupled with acids tend to form a reversible ionic liquid-like adduct by capturing the proton of the acid into the imidazolium moiety. Complexation between carboxylic acid and imidazoles involves proton transfer or/and hydrogen bonding formation and generates enough heat to make the reaction exergonic. The complexation step must possess relatively low bond energy for it to be economically attractive. It has been reported that complexation reactions with bond energies less than 50 kJ/mol are similar to ordinary association by van der Waals forces in the condensed state and can be readily reversed, while those with bond energies exceeding 50 kJ/mol are difficult to reverse and hence give rise to higher costs [8]. Extensive research has been conducted on the interaction between carboxylic

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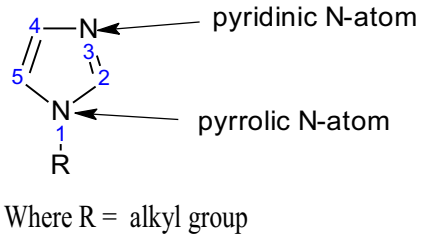
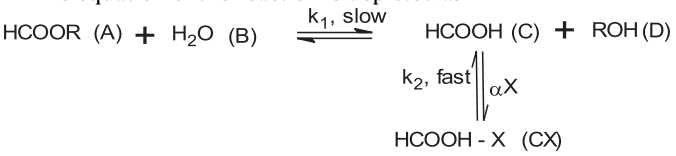


Scheme 1. Structure of 1-alkylimidazoles.

acid and amine in an analogous process such as reactive extraction [9–11]. Salman and co-workers [12] studied the reaction enthalpy between N′,N′,N′,N′-tetramethylethylenediamine and formic acid with regards to energy storage. The nature of hydrogen bonding and enthalpy of complex formation between 1-alkylimidazoles and some carboxylic acids were investigated by Reinhardt et al. [13] whereas Schaub and Paciello [14] demonstrated the thermodynamic role of solvent in the synthesis of formic acid via carbon dioxide hydrogenation in the presence of a base. Although, these aforementioned studies are not the same as the hydrolysis-complexation process in terms of methodology and end results, what they have in common is the complexation process. The objective of this work is to study the complexation equilibria of alkyl formate hydrolysis in the presence of 1-butylimidazole and evaluate the thermodynamic parameters of the reaction. The nature of the interaction between the acid and the base using Fourier Transform Infrared (FTIR) is also included in the study.

2. Complexation equilibria

The equation of the reaction is depicted as



where R = CH_3 or C_2H_5, X = complexing agent and HCOOH–X = acid–base complex and α = stoichiometric coefficient of the complexing agent.

In the hydrolysis-complexation process (HCP), the complexing agent is a base, which interacts with only the acid product and forms a reversible ion pair. It is pertinent to state here that the value of α is not always unity but strongly depends on the nature of the complexing agent and the acid-base interaction, which in turn, is a function of the complexing agent concentration. The equilibrium constant for the complex formation (K_2) between formic acid and 1-butylimidazole (X) can be expressed as

$$K_2 = \frac{C_{CX}}{C_C * (C_X)^{\alpha}} \tag{1}$$

The most useful quantitative indication of the tendency to undergo electrophilic attack at the N-3 position is provided by the pK_a values. In order to quantify the acid-base interaction (i.e. describe the complexation constant), knowledge of the dissociation constant of both the formic acid (pK_a = 3.74) and the complexing agent (pK_a = 7.21) are important [7]:

$$\log K_2 = pK_{a,X} - pK_{a,\mathrm{HCOOH}} \quad \text{for which} \quad \alpha = 1 \tag{2}$$

As a guide, the value of K_2 signifies whether the complexation reaction will go to completion or not as well as the stability of the complex. The value of pK_a of the anion of a potential complexing agent must be larger than that of the acid in order to have a significant complex formation. Furthermore, the stability of the complexing agent in the acidic medium is quite important for process intensification because the pH of the solution decreases as the reaction goes towards equilibrium. The equilibrium constant for the hydrolysis step at zero concentration of X (i.e. in the absence of the complexing agent) is expressed as

$$K_1 = \frac{C_C C_D}{C_A C_B} \tag{3}$$

When a suitable complexing agent is added, it picks up C only and there is an increase in the yield of the products as soon as more A and B react. Thus, the apparent formation constant, when activity coefficients are approximated to unity, is [15]

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

C^* represents the new concentration due to the presence of the complexing agent in the solution. $K_{1,app} > K_1$ since component C is bound to X. The fraction of the free formic acid in the solution may be represented as

$$p_C = \frac{K_1}{K_{1,app}} = \frac{C_C}{C_C^*} = \frac{C_C}{C_C^T} \tag{5}$$

Thus, $p_{CX} = 1 - p_C = \frac{C_{CX}}{C_C^T}$. Let $q = C_C^T/C_X^0$, $C_C^T = C_C + C_{CX}$, where C_C^T is total concentration of the acid, consisting of both dissociated (CX) and free molecules (C), while C_X^0 is the initial concentration of the complexing agent. Also, q is the complexation factor that describes the ratio of all the species that contained the acid to that of the initial concentration of the base.

The stoichiometric relation between the acid and the complexing agent gives

$$C_X = C_X^0 - \alpha C_{CX} \tag{6}$$

Substituting for the values of C_C and C_X in Eq. (1), we obtain

$$K_2(C_X^0 - \alpha C_{CX})^{\alpha} = \frac{C_{CX}}{(C_C^T - C_{CX})}$$

$$K_2(C_X^0)^{\alpha}\left(1 - \frac{\alpha C_{CX}}{C_X^0}\right)^{\alpha} = \frac{\frac{C_{CX}}{C_C^T}}{\left(1 - \frac{C_{CX}}{C_C^T}\right)}$$

$$K_2 = \frac{p_{CX}}{(C_X^0)^{\alpha}(1 - p_{CX})(1 - \alpha q p_{CX})^{\alpha}} \tag{7}$$

It can be deduced from Eq. (7) that the complexation constant depends on the acid–base interaction, which is a function of C_{0X}. If α is unity, Eq. (7) becomes

$$K_2 = \frac{p_{CX}}{(C_X^0)(1 - p_{CX}) * (1 - q p_{CX})} \tag{8}$$

In the absence of a reliable analytical procedure for the determination of C_{CX}, which is true in our case, the values of C_{CX} can be estimated from the following expressions:

Recall from Eq. (5) that $K_1/K_{1,app} = C_C/C_C^*$, then putting in the value of $K_{1,app}$ into Eq. (4), we have

$$C_C = \frac{K_1 C_A^* C_B^*}{C_D^*} \tag{9}$$

Then,

$$C_{CX} = C_C^T - C_C \tag{10}$$