

ION EXCHANGE RESIN-CATALYSED ESTERIFICATION OF ALIPHATIC AND AROMATIC ACIDS WITH METHANOL AND ETHANOL

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(Received September 16, 1984; revised October 15, 1985)

Studies have been made on the kinetics of the esterification of methanol and ethanol with various types of organic acids using the *m*-cresol-formaldehyde ion exchange resin as a catalyst. The influence of molecular weight and structure of the acids on the conversion has been investigated. The experimental data was found to fit a second order bimolecular kinetic equation. The rate constant (K_1) for nine organic acids has been calculated. The velocity constant was found to bear linear relationship with the molecular weight of the acids under investigation.

INTRODUCTION

The heterogeneous catalytic esterification of alcohols with organic acids in the presence of cation exchange resin in the H^+ - form has been widely reported [1-5]. A few investigations of catalytic reactions concerning the effect of molecular weight and structure of organic acids and alcohols on the rate of esterification have been published [4, 5]. For example, Karpov [5] studied the effect of the structure of alcohols by using different types of alcohols, $C_n H_{2n+1} OH$, ($n = 4, 5, 6, 7$). The reaction rate was found to decrease as the alcohol chain length or branching increases. The same author [5] also studied the esterification of amyl and *iso*amyl alcohols with organic acids, $R. COOH$, ($R = Pr, Bu$). It was deduced that the rate of reaction decreased markedly as the branching of the side chains of both acids and alcohols increases.

In this paper we report the effect of molecular weight, branching, number of carboxylic acid groups and type of acid (aliphatic or aromatic) on the rate of the esterification of methanol and ethanol in the presence of synthetic ion exchange resin as a catalyst.

MATERIALS AND METHODS

All the chemicals used in this study were either BDH (Analar) or E-Merck (GR) grade.

The catalyst used in this study was of *m*-cresol formaldehyde sulphonic acid resin with an exchange capacity of 2.2. 2 meq./g. of dry resin. It was prepared by the method described by Hassan *et al.* [7].

The reaction was carried out in a three-necked one litre flask placed in a constant temperature bath. The acid and

a portion of the alcohol were charged into the flask. The contents were kept thoroughly agitated for few minutes and lastly the catalyst and the remaining alcohol were added. Samples were taken out at regular intervals for subsequent analysis using 0.1 N sodium hydroxide solution.

RESULTS AND DISCUSSION

Effect of molecular weight of acid. The influence of molecular weight of a homologous series of organic acids (acetic, propionic, butyric and valeric) on the rate of the esterification of methanol and ethanol was studied in presence of the cation exchange resin as catalyst. The amount of the acid was chosen to give a constant molar ratio of alcohol/acid = 24.74, and the quantity of alcohol was in all cases in excess, i.e. of the order of 200 ml. The effect of the molecular weight of the above mentioned acids on the fractional conversion of acid is shown in Fig. 1 and 2. The fractional conversion of different acids, using the same alcohol, decreased as the molecular weight of acid increases. The rate of esterification of a given acid was found to be dependent markedly on its molecular weight. The reaction velocity constant (k_1) was calculated using the linear transformation of Fig. 1a and 2a. The data obtained were found to fit a second order bimolecular equation [3, 6] of the type:

$$\log \frac{X_{eg} - X_A}{X_{Ae} - X_A} \frac{X_{Ae}}{X_{eg}} = \frac{2B - (B+1) X_{Ae}}{X_{Ae}} k_1 C_{Ao} t$$

with the plotting of $\log \frac{X_{eg} - X_A}{X_{Ae} - X_A}$ against (t), a linear relationship (Fig. 1a and 2a) results.

The experimental conditions used in this study and the values (k_1) obtained are given in Tables 1 and 2.

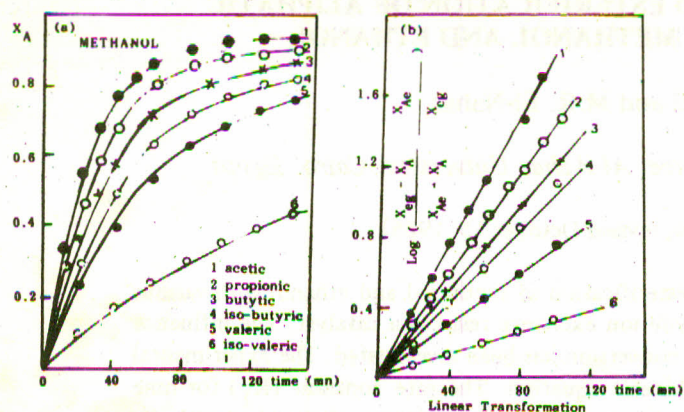


Fig. 1. Effect of molecular weight of acid on X_A

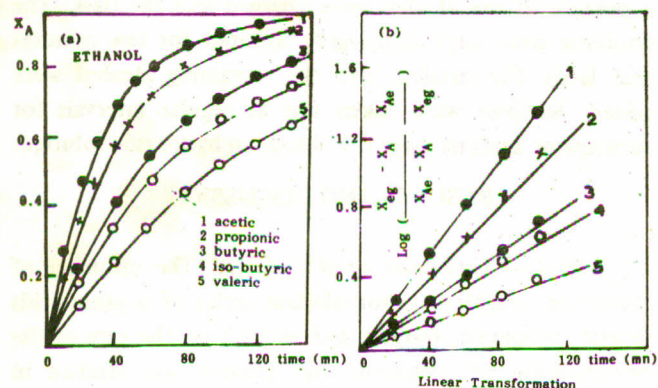


Fig. 2. Effect of molecular weight of acid on X_A

It is of interest to note that when the k_1 value are plotted against the corresponding molecular weights of the acid, good straight lines were obtained, whatever the type of alcohol used, (Fig 3 and 4). It is clearly seen from Tables 1-2 that the values of k_1 decrease by increasing the molecular weight of organic acid. Moreover, many other alcohols (e.g. propanol, butanol, *isopropanol* and *isobutanol*) were also used with the same series of homologous organic acids. A linear relationship between k_1 values and the molecular weights of acids was obtained [8].

It must be noted that the values of k_1 obtained in the case of *isobutyric* and *isovaleric* acids do not coincide on the straight line, although they have the same molecular weight of the corresponding normal acids (Fig. 3 and 4). The slow rate of esterification of these branched acids can be easily attributed to both steric hindrance and the inductive effect exhibited by the alkyl groups.

The results presented here clearly show that the rate of esterification is strongly influenced by variation in chain length (mol. weight), or the branching of both acid

Table 1. Reaction velocity constant for the esterification of different organic acids with methanol.

Run No.	Acid	Mol. wt. of acid	$k_1 \times 10^5$	X_{Ae}
1.	Acetic	60	3.354	0.95
2.	Propionic	74	2.508	0.93
3.	Butyric	88	1.991	0.90
4.	<i>isobutyric</i>	88	1.576	0.86
5.	Valeric	102	1.164	0.85
6.	<i>isovaleric</i>	102	0.468	0.73

$$C_{A0} = 0.839 \text{ mole/l} \quad B = 24.74 \quad W = 5.87 \text{ g} \quad T = 336^\circ\text{K}$$

Table 2. Reaction velocity constants for the esterification of different organic acids with ethanol.

Run No.	Acid	Mol. wt. of acid	$k_1 \times 10^5$	X_{Ae}
1.	Acetic	60	3.330	0.94
2.	Propionic	74	2.526	0.92
3.	Butyric	88	1.603	0.90
4.	<i>isobutyric</i>	88	1.158	0.885
5.	Valeric	102	0.869	0.881

and alcohol. These results are in good agreement with the work of Karpov [4, 5]. On the other hand, Karpov [4, 5] did not report any kinetic expression for the correlation of his data.

Effect of the structure of acids. From the present work as well as in other studies, [3, 5] it can be deduced that the rate of esterification of linear acids is high compared with that of the branched ones. It is of interest to study the effect of varying the number of $-\text{COOH}$ groups in a given acid on the rate of esterification. The k_1 values

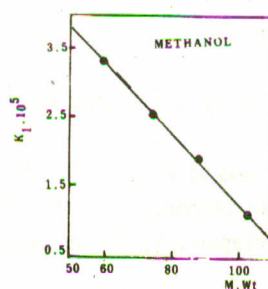


Fig. 3. Effect of molecular weight of acid on K_1

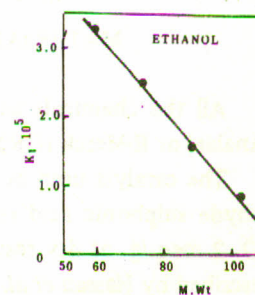


Fig. 4. Effect of molecular weight of acid on k_1

obtained for the esterification of adipic acid $\text{HOOC}-(\text{CH}_2)_4-\text{COOH}$ and valeric acid $\text{CH}_3-(\text{CH}_2)_3-\text{COOH}$ with methanol were compared (Table 3). Although the dicarboxylic acid has a lower molecular weight, its k_1 value was found to be greater than that of the monocarboxylic acid. This inverse result could be explained on the basis that the presence of two carboxylic groups in adipic acid gives it good chance for further esterification to proceed. As seen from Fig. 5 and Table 3, similar results were obtained by

Table 3. Reaction velocity constants for the esterification of some aliphatic and aromatic acids with methanol.

Run No.	Acid	Mol. wt. of acid	$K \times 10^5$	X_{Ae}	t. for attain eqb. (mn)
1.	Adipic	146	1.307	0.90	140
2.	Oxalic	126	0.699	0.38	120
3.	Benzoic	122	0.221	0.17	360
4.	Phthalic	166	0.342	0.25	360

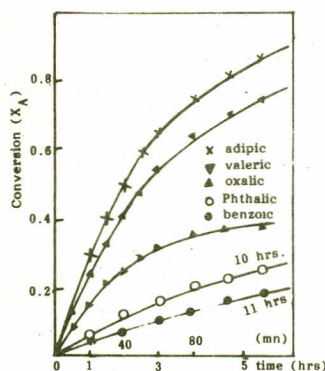


Fig. 5. Effect of number of (COOH) groups on conversion

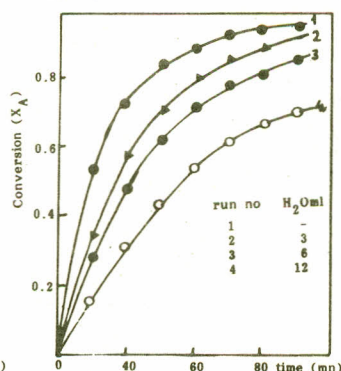


Fig. 6. Effect of water concentration on conversion

using aromatic acids (benzoic and phthalic). The comparison of the k_1 values for both aliphatic and aromatic acids showed that the rate constant of aliphatic acid are of much higher magnitude than those of aromatic ones. This is probably due to the presence of aromatic ring exhibiting steric hindrance on the course of the reaction.

The esterification of oxalic acid $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ with methanol was also studied, and the reaction velocity constant (k_1) was evaluated and compared with that of adipic acid. Table 3 indicates that the k_1 value of oxalic acid is smaller than that of adipic acid, although the former has a smaller molecular weight. This retardation effect is probably due to the presence of two molecules of water of crystallization in the oxalic acid molecule which enhanced the resin-water interaction, thus forming H-bonded mole-

cules. This water-resin interaction inhibited to some extent the esterification reaction [1, 9]. This assumption was tested by the addition of increasing amounts of water to the reaction medium in the case of the esterification of butyric acid with methanol, (Fig. 6). It is interesting to report that the decrease of the rate of esterification with increasing water content is due in part to the decrease of the reaction temperature [9].

CONCLUSIONS

The general picture that emerges from these kinetic studies can be summarized as following:

1. The rate of the esterification of organic acid is inverse-ly proportional to its molecular weight.
2. The reaction velocity constant of dicarboxylic acid (aliphatic or aromatic) is higher than that of monocarboxylic acids.
3. In general, the rate of esterification of an aliphatic acid is greater than that of an aromatic one.
4. Branched acids exhibit slower rate of esterification than corresponding linear acids.
5. The presence of water of crystallization in the organic acid molecule, as well as the addition of water to the reactants has a retarding effect on the overall rate of esterification.

NOMENCLATURE

- B = Initial mole ratio of alcohol/acid.
 C_{Ao} = Initial concentration of the acid, g mole/l.
 K_1 = Reaction velocity constant, 1 litre g mole⁻¹ sec⁻¹.
 m_{eq} = H^+ -concentration, meq/100 g reactants.
 t = Time in sec.
 T = Temperature, °K
 X_A = Fraction conversion of acid.
 X_{Ae} = Equilibrium conversion of acid.
 X_{eg} = Constant, given by $X_{eg} = \frac{BX_{Ae}}{(B+1)X_{Ae} - B}$
 W = g. catalyst/100 g reactants.

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