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# Esterification of Some Organic Acids with Isopropanol Catalysed by Cation Exchange Resin: Styrene Butadiene Phenolformaldehde

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The esterification of various organic acids with isopropanol have been studied in presence of styrene butadiene phenolformaldehyde sulphonic group as a catalyst. The data for the rate constant are correlated to the second order bimolecular reversible reaction. For the esterification of acetic acid with isopropanol especially; the effect of molar ratio of reactants, reaction temperatures, amount of catalyst and of percent of added water on the reaction rate constant and on the percent conversion were studied. A linear relationship was obtained from the plots of log specific rate constant against molecular weight of the used carboxylic acids, amounts of catalyst, but is reciprocal of temperature. The values of $\Delta G^*$, $\Delta H^*$ and $\Delta S^*$ were calculated at each temperature and compared.

## INTRODUCTION

Several authors[1,2] have investeigated the esterification of organic acids in presence of mineral acids as a catalyst, such as HCl and $H_2SO_4$. The heterogeneous catalytic esterification of organic acids with alcohols is found to have several advantages.[3,4] Bochner *et al.*[5] found that the rate of conversion of salicyclic acid to methyl salicylate (ester) in presence of HCR-W2 cation exchanger is not affected by stirring rate, catalyst particle size, or extent of reverse reaction. Upon esterification of oleic acid as a long chain molecule with butanol in presence of cation exchange resin, that the reaction rate is proportional to the external surface area of the particles and that the slow diffusion rate. Owing to the large molecule of the acid, appears to occur only at or near the surface of the resin particles.[6] The values of the specific rate constant $k_1$ were determined using an empirical correlation, incorporating the effect of the $H^+$-concentration of the catalyst and of the reaction temperature on the reaction velocity constant.[7]

The aim of the present work is to investigate the esterification reactions of some organic acids; formic, acetic, propionic, butyric, valeric, isovaleric and oleic acids in presence of styrene butadiene phenolformaldehyde cation exchanger ($H^+$-form). The effects of amount of catalyst of the resin, temperature of reaction, molar ratio of reactants and the addition of water on the percent of conversion were evaluated. The thermodynamic parameters i.e. $\Delta E^*$, $\Delta G^*$, $\Delta S^*$ and $E^*$ were also calculated for the reaction factor.

## EXPERIMENTAL

All chemicals used were of either BDH (AnalaR) or E-Merck (GR) Grade. The synthesized cation exchanger (Styrene butadiene phenol-formaldehyde)[8]; cap. 3.4 milliequivalent/g dry resin. The esterification reaction was carried out in a three-necked flask equipped with a stirrer, reflux condenser and thermometer and placed in a bath thermostated at the desired temperature. The flask was initially charged with a portion of studied alcohol followed by addition of the whole calculated amount of acid and stirring for *ca* 20 min. The catalyst and the remainder of the alcohol was then added under stirring at the desired temperature. The contents were kept thoroughly agitated for few minutes and lastly the catalyst were taken out at regular intervals for subsequent analysis using 0.1 N sodium hydroxide solution as well as the method was studied earlier[7].

## RESULTS AND DISCUSSION

The results of the values found for the fractional conversion, reaction velocity constant $k_l$ and percent conversion at equilibrium are found to depend upon the nature of acid used (Table 1). These values were found to decrease with increasing of molecular weight, chain length and branching of the reacting acid.

TABLE 1

REACTION VELOCITY CONSTANT FOR ESTERIFICATION REACTION OF ACIDS WITH ISOPROPANOL

| Acids | $k_1 \times 10^5$ specific rate consttant | $X_{Ae}$;% | $\Delta$G* K. cal/mol |
|---|---|---|---|
| formic | 4.552 | 85.1 | 29.622 |
| acetic | 4.101 | 81.6 | 29.700 |
| propionic | 3.510 | 77.4 | 29.776 |
| butyric | 2.718 | 69.0 | 30.007 |
| valeric | 2.150 | 39.0 | 30.182 |
| isovaleric | 1.655 | 32.0 | 30.377 |
| oleic | 0.082 | 16.0 | 30.832 |

The values of $\Delta G^*$ for all esterification reaction of acids have been shown to be positive and in increasing order with increase in molecular weight of acids. The results are given in Table 1, indicating that the esterification reaction of the used acids becomes slower at higher molecular weight, *i.e.* oleic acids. Plotting of the values for the specific rate constant $k_1$ against molecular weight of the used acids gave a linear relationship, (Fig. 1).

The increase in the values of percent conversion and of specific rate constant $k_1$ with the increase in the amount of added catalyst in the esterification reaction of acetic acid with isopropanol, the data given in Table 2

TABLE 2

REACTION VELOCITY CONSTANT $k_1$ AND $X_{Ae}$ FOR THE ESTERIFICATION REACTION OF ACETIC ACID WITH ISOPROPANOL

*Effect of molar ratio of reactants* (10 g) *at 85°C*

| Molar ratio; B | Reaction velocity constant; $k_1 \times 10^{-5}$ | $X_{Ae}$; % | $\Delta G^*$ Kcal./mol |
|---|---|---|---|
| 3 | 3.77 | 83.0 | 28.128 |
| 5 | 3.98 | 83.5 | 28.089 |
| 8 | 4.10 | 85.1 | 28.068 |

*Effect of temperature at B = 8 and catalyst = 10 g*

| Temp., C° | Reaction velocity constant; $k_1 \times 10^{-5}$ | $X_{Ae}$ % | $\Delta G$ Kcal./mole | $\Delta H^*$ | $\Delta S^*$ |
|---|---|---|---|---|---|
| 60 | 2.75 | 71.0 | 26.513 | 3.953 | −0.0637 |
| 70 | 3.21 | 79.5 | 27.224 | 3.913 | −0.0639(5.277) |
| 82.5 | 4.10 | 85.1 | 28.068 | 3.864 | −0.0641 |

*Effect of amount of catalyst at B = 8 and temp., 82.5°C*

| Amount of catalyst | Reaction velocity constant $k_1 \times 10^{-5}$ | $X_{Ae}$; % | $\Delta G^*$ Kcal/mole |
|---|---|---|---|
| 4 | 2.05 | 72.0 | 28 558 |
| 6 | 2.98 | 77.0 | 28.294 |
| 8 | 3.55 | 81.0 | 28.173 |
| 10 | 4.10 | 85.1 | 28.068 |

*Effect of added water at B = 8, temp. 82.5°C and Resin* = 10 g

| Amount of added water | Reaction velocity constant; $k_1 \times 10^{-5}$ | $X_{Ae}$; % | $\Delta G^*$ Kcal/mole |
|---|---|---|---|
| 4 | 2.95 | 78.0 | 28.301 |
| 8 | 2.01 | 70.5 | 28.572 |
| 10 | 1.65 | 61.3 | 28.711 |

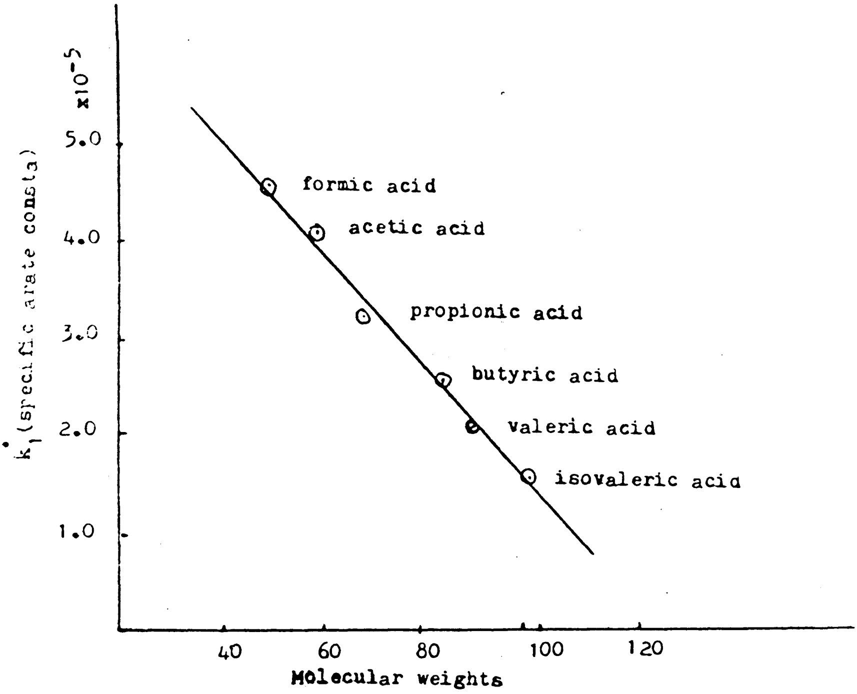

Fig. 1 Plots of $k_1$ aganist molecular weights

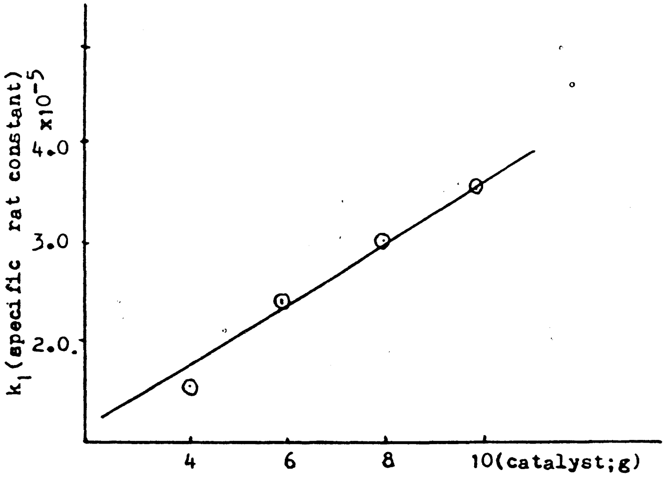

Fig. 2 Plots of $k_1$ against amount of catalyst

and Fig. 2 could be attributed to the increase in the $H^+$-ion concentration in the resin. Table 2 also shows that the percent conversion as well as the values of specific rate constant increase slightly with the molar ratio of reactants and increase markedly with temperature.

The decrease in the values of specific rate constant with increasing amount of water to the reaction (Table 2), could be explained as being due to the association of water molecules with network of the resin, and resulting in a deactivation effect of H$^+$-ion, with catalyst effect in the forward reaction.[9]

## Correlation of the Rate Data

The specific rate constant $k_1$ for the esterification of the used acids with isopropanol was calculated, using the simplified equation propossed by Sharma *et al.*[4]

$$\ln \frac{X_{eg} - X_A}{X_{Ae} - X_A} \cdot \frac{X_{Ae}}{X_{eg}} = \frac{2B - (B + 1)X_{Ae}}{X_{Ae}} k_1 C_{A_0} \qquad (1)$$

where

$$X_{eg} = \frac{BX_{Ae}}{(B + 1)\, X_{Ae} - B}$$

By plotting:

$\ln \frac{X_{eg} - X_A}{X_{Ae} - X_A} \cdot \frac{X_{Ae}}{X_{eg}}$ *vs.* time *t*, the obtained experimental data found to fit fairly the rectilinear relation, representing that the esterification of isopropanol with the studied acids, in the presence of styrene butadiene phenolformaldehyde exchanger (SO$_3$H$^+$-group), is a second order bimolecular reversible reaction (Fig. 3). Plotting the values of log $k_1$ against the

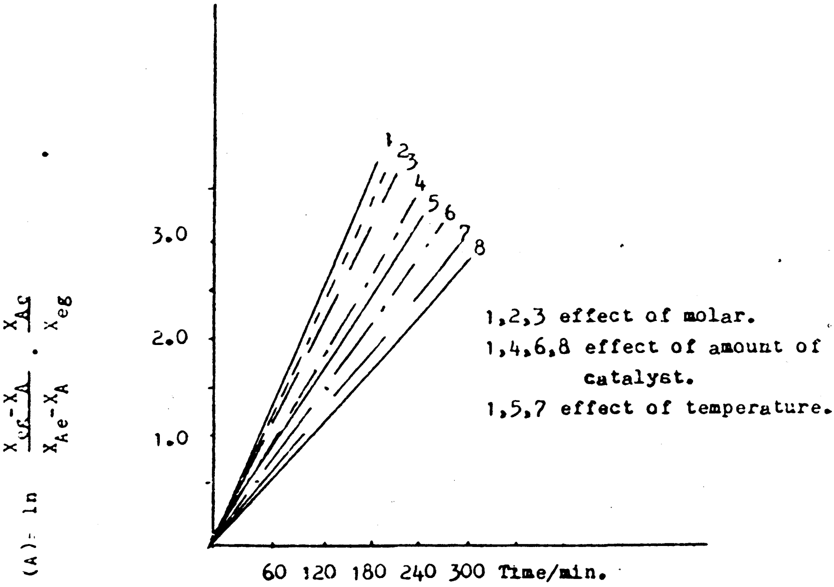

Fig. 3. Plots of (A) against time *t*

amount of catalyst, addition of water, and also against the reciprocal of temperature $1/T$ gave a rectilinear relation (Fig. 4).

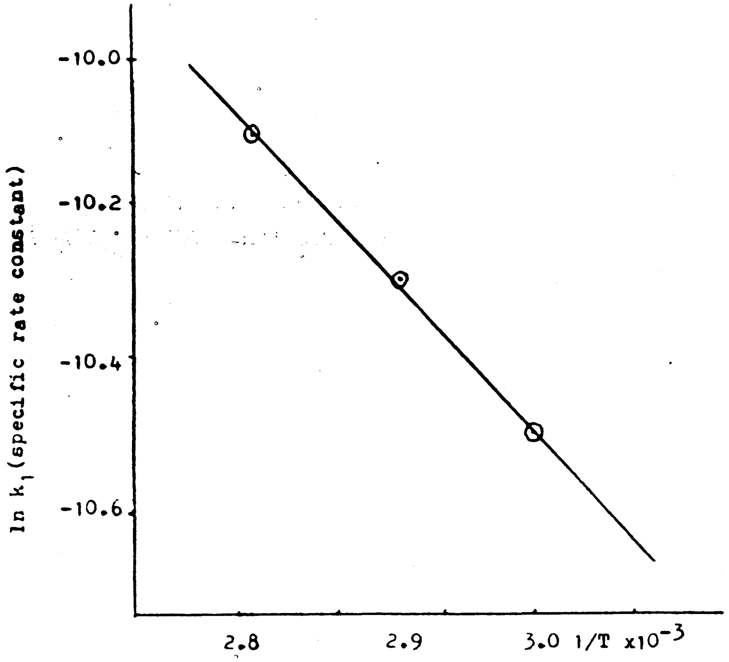

Fig. 4 Plots of in $k_1$ against $1/T$

The values of $X_{Ae}$ (the conversion of the esterification reaction of the used alcohol with acetic acid is obtained either experimentally when the equilibrium is attained or by fitting[4] the experimental data using equation 2

$$X_A = X_{Ae}\,[1 - e^{-ht}] \tag{2}$$

The values of $X_{Ae}$ were assumed and log $(X_{Ae} - X_A)$ was plotted against time $t$. The correct value of $X_{Ae}$ is obtained, when the assumed value and that obtained from the intercept of the linear plot coincide.

It is of interest to interpret the data calculated in the present study in terms of the values of the activation terms $E^*$; was determined from Arrhenius plot Table 2. $\Delta H^*$ the change of enthalpy of activation was obtained from the equation.[10]

$$H^* = E^* \text{ (activation energy)} - nRT \tag{3}$$

The free energy change of activation was obtained from Eyring's equation (1).

$$k_1 = \frac{kT}{h} \exp\,(-\Delta G^*/RT) \tag{4}$$

where $k_1$, is the rate constant, $k$ Boltzmann constant, $h$ Planck's constant.

The final parameter $\Delta S^*$ (the entropy of activation) has been calculated using the following relation.

$$\Delta S^* = \frac{\Delta H^* - \Delta G^*}{T^0} \tag{5}$$

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### हिन्दी साहित्य सम्मेलन, प्रयाग द्वारा
### ९–१० मार्च १९९१ को रोहतक में विज्ञान गोष्ठी का आयोजन

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