A Study on Catalyzed Azeotropic Esterification

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The homogeneous and heterogeneous catalyzed azeotropic esterifications of benzoic and oleic acid with butanol have been investigated. After an initial period, the reactions follow a bimolecular kinetics. The effect of the distillation rate on the process rate is attributed mainly to the variation of the reaction temperature.

INTRODUCTION

Because esterification is an equilibrium reaction, various esterification methods in which the equilibrium is displaced by removal of one of the reaction products has been developed. One way of completing the esterification is to distil out the water produced in the reaction as an azeotrope with one of the components of the reaction mixture. The vapor phase is condensed and the two phases separate in a receiver. The nonaqueous phase returns to the esterification vessel by an overflow and the aqueous phase is withdrawn from the bottom of the receiver (*1*).

In the elimination of water from reaction mixtures by azeotropic distillation with inert solvents, the heat input to the heater unit, i.e., distillation rate, has been found influencing the process rate (*2–5*); the simultaneous heat and mass transfer in evaporation has been considered as the last step of consecutive ones through which the process occurs. A marked effect of distillation rate on azeotropic esterification has been reported in a previous paper, where the esterification of oleic acid with butanol catalyzed by a cation-exchange resin has been investigated (*6*); both water concentration and temperature of reaction mixture were dependent on distillation rate.

In the present paper some results concerning the homogeneous and heterogeneous catalyzed azeotropic esterifications of ben-zoic and oleic acid with butanol are reported and the role played in the process by the distillation rate is studied.

EXPERIMENTAL METHODS

Procedure. Butanol, organic acid, and catalyst, the amount of which are reported in Table 1, were placed in a 1-liter flask fitted with stirrer, thermometer, and reflux condenser with water separator and heated at reflux for the duration of the experiment. The heat input to the heater unit was controlled by a Variac and its measurement based on the determination of the distillation rate of butanol, i.e., expressed by moles of butanol evaporated in 1 hr. The pressure was regulated by a manostat. Zero

TABLE 1
AMOUNTS OF REACTANTS AND CATALYST
CHARGED TO THE FLASK

Butyl benzoate
Butanol = 3.82 moles
Benzoic acid = 0.89 moles
Homogeneous catalysis: amounts of H_2SO_4 corresponding to 3.49, 6.55, 13.10, 26.21 mmoles of H^+
Heterogeneous catalysis: amounts of resin corresponding to 6.28, 12.19, 25.59 mmoles of H^+
Butyl oleate
Butanol = 3 moles
Oleic acid = 0.7 moles
Homogeneous catalysis: amount of H_2SO_4 corresponding to 0.47 mmoles of H^+
Heterogeneous catalysis: amount of resin corresponding to 12.19 mmoles of H^+
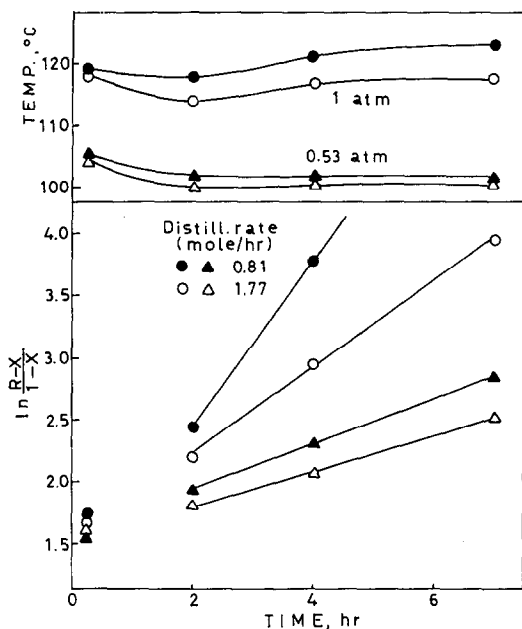
FIG. 1. Homogeneous catalysis of butyl benzoate: conversion of benzoic acid to butyl benzoate and temperature of reaction mixture vs time; amount of catalyst $=$ 13.10 mmoles of H^+.

time was taken as the time when refluxing started.

Analytical. A portion of the reaction mixture was removed from the flask with a pipet and the acid was determined by titration with 0.1 N sodium hydroxide solution.

Materials. The reactants: butanol, benzoic and oleic acid were Carlo Erba products. The heterogeneous catalyst was a cation-exchange resin: 32–48 and 100–250 mesh Dowex 50W X2. The resin was employed wet (dried on filter paper), containing 79.2 wt % H_2O.

BUTYL BENZOATE

The conversion of benzoic acid to butyl benzoate and the temperature of the reaction mixture are plotted against the time in Figs. 1 and 2 for homogeneous and heterogeneous catalyzed esterification, respectively ($R =$ initial butanol/benzoic acid molar ratio in the charge, $X =$ conversion, $t =$ reaction time). Experiments have been carried out on reaction mixtures boiling at reflux at different pressures to ex-
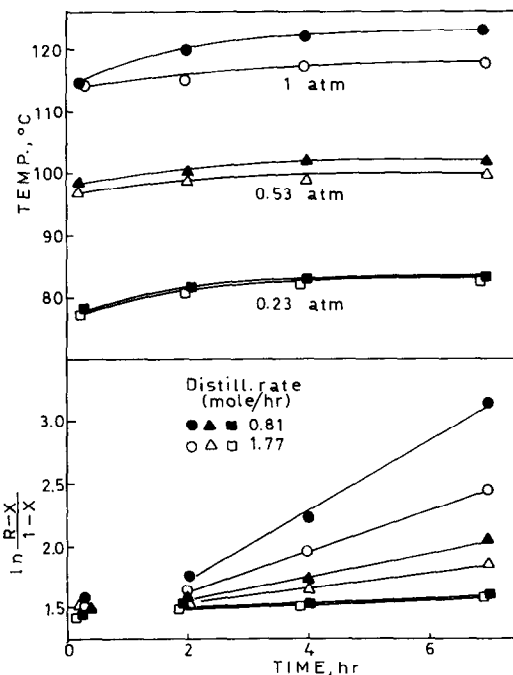

FIG. 2. Heterogeneous catalysis of butyl benzoate: conversion of benzoic acid to butyl benzoate and temperature of reaction mixture vs time; amount of catalyst $=$ 12.19 mmoles of H^+; catalyst size $=$ 32 – 48 mesh; and stirring rate $=$ 260 rpm.

amine the process at different temperature ranges.

Generally, after the first steps of reaction, the temperature assumes with time values which may be considered nearly constant, at least for the duration of runs, so that the data in the last 5 hr fit fairly well a bimolecular kinetic equation. The failure of the second order kinetics to hold over a slow initial period has been reported by Levesque and Craig (7) in the esterification of oleic acid with butanol with a cation-exchange resin catalyst and attributed to the variations of water concentration and temperature of the reaction mixture (6).

The effect of the reverse reaction has been investigated by preaddition of butyl benzoate to the starting mixture. It must be pointed out that the amount of ester in the charge gave no appreciable effect on the reaction temperature. As visualized in Fig. 3, the rate of the reverse reaction appears
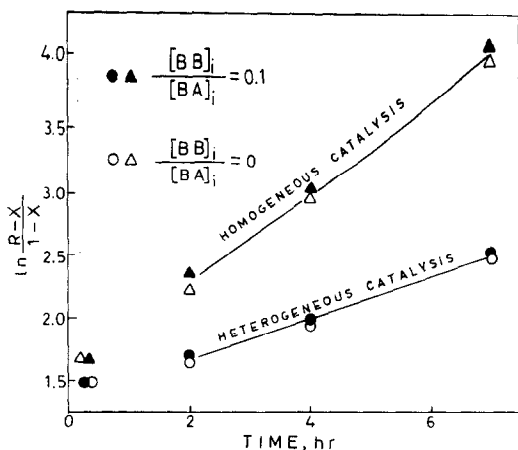
FIG. 3. Butyl benzoate: effect of reverse reaction. $[BB]_i/(BA]_i$ = initial butyl benzoate/benzoic acid molar ratio in the charge; amount of catalyst = 13.10 mmoles of H^+ (homogeneous catalysis), 12.19 mmoles of H^+ (heterogeneous catalysis); catalyst size = 32–48 mesh; stirring rate = 260 rpm; distillation rate = 1.77 mole/hr; and boiling pressure = 1 atm.

to be negligible in the process. The last behavior has been found by Bochner *et al.* (*8*), who studied the esterification of salicylic acid with methanol catalyzed by a cation-exchange resin.

As regards the heterogeneous catalysis, the effects of stirring rate and particle size on the rate of formation of butyl benzoate has been investigated. Figure 4 shows
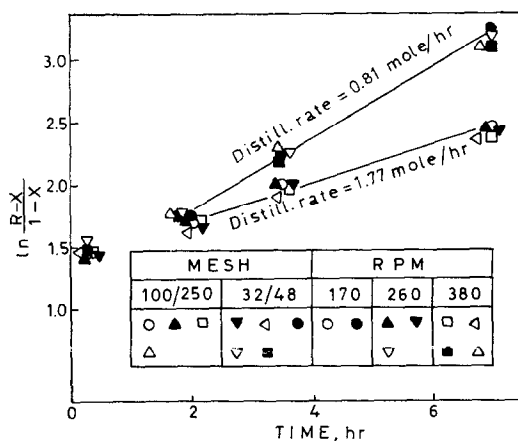

FIG. 4. Heterogeneous catalysis of butyl benzoate: effect of agitation and catalyst particle size; amount of catalyst = 12.19 mmoles of H^+; and boiling pressure = 1 atm.

plainly that the rate of conversion is practically unaffected by stirring rate and catalyst particle size, i.e., both bulk and intra-particle diffusional phenomena are not limiting. Therefore, the chemical regime must be considered controlling in the heterogeneous catalyzed esterification.

From Figs. 1 and 2 the values of the esterification rate constant are obtained

$$K' \equiv \frac{d \ln[(R - X)/(1 - X)]/dt}{C_0(R - 1)} \left(\frac{\text{liter}}{\text{mole} \times \text{hr}}\right)$$

from the slope of the plot of $\ln (R - X)/(1 - X)$ against t (C_0 = initial concentration of benzoic acid). They are very closely proportional to the ratio of the number of moles of catalytic hydrogen ions to the volume of solution so that the specific esterification rate constant may be introduced:

$$K = K'/[H^+] \left(\frac{[\text{liter}]^2}{[\text{mole}]^2 \times \text{hr}}\right).$$

In Figs. 1 and 2, the effect of the distillation rate is also presented. The lower both temperature range and specific rate constant are obtained with the higher distillation rate. This behavior must be considered specific of the azeotropic esterification which is carried out with condensation of the mixed water–butanol vapors, separation of the aqueous phase and reflux of the non-aqueous phase into the reaction vessel. In such conditions, the temperature and composition of the reflux mixture is dependent on the condensate loading, i.e., distillation rate. The higher is the condensate loading, the higher are both the temperature of the overflow and its water content, as reported in the previous paper (*6*). According to the higher reflux rate of water into the flask, the content of water in the reaction mixture increases with lowering of reaction temperature. The effect of the distillation rate is the more emphasized the higher is the boiling pressure.

The specific rate constants have been calculated in the last 5 hr of the runs and reported against the temperature, which has been averaged in this period on the Arrhenius plot (Fig. 5). It yields a straight line; therefore, the temperature of the reac-
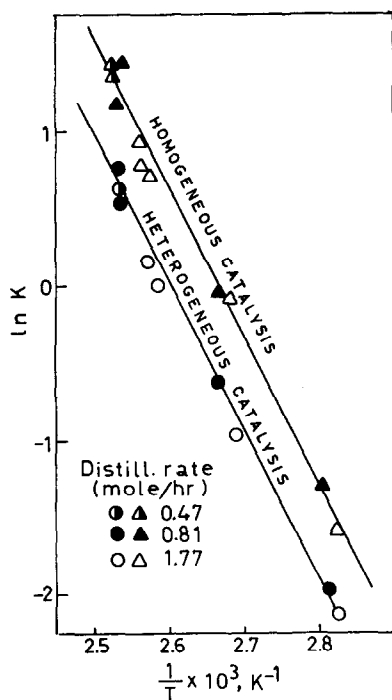
Fig. 5. Butyl benzoate: Arrhenius plot.

Fig. 6. Butyl oleate: Arrhenius plot.

tion mixture may be assumed to correlate results which have been obtained at different distillation rates and the simultaneous heat and mass transfer in evaporation, which follows the reaction step, may be considered not limiting.

Both the homogeneous and heterogeneous catalyzed esterifications have very closely the same activation energy, $E_0 \simeq 18$ kcal/mole, and the reaction rate is less when the catalyst is an ion-exchange resin than when it is homogeneously dissolved in equivalent amount. The last behavior may be attributed either to a loss in internal entropy of the reactants which accompanies their fixation on the skeleton of the resin catalyst in the formation of the transition state (9) or to a different repartition of the reactants between the pore liquid and the supernatant solution according to the Helfferich's standpoint (10).

BUTYL OLEATE

Levesque and Craig (7), investigating the effect of the resin particle on the esterification rate, deduced that the reaction, owing to the slow diffusion rate of the large
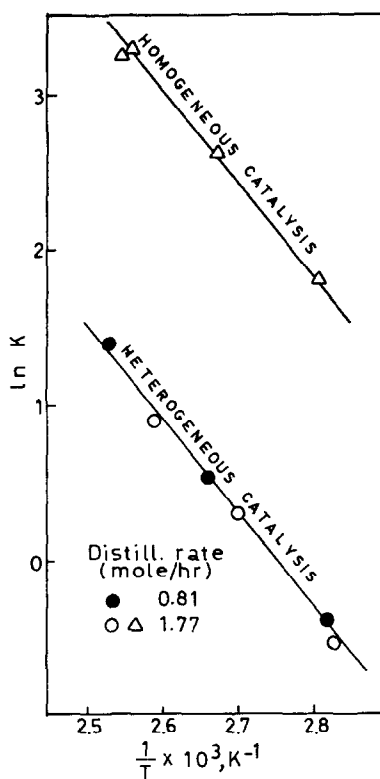
molecule of the oleic acid, occurs only at or very near the surface of the catalyst. On the contrary the bulk diffusion has been found not rate limiting (11).

Extending the previous results (6), runs at different boiling pressures and distillation rates have been carried out. The conversion of oleic acid to butyl oleate and the mixture temperature against the reaction time for both homogeneous and heterogeneous catalyzed esterifications are in qualitative agreement with those concerning butyl benzoate. Likewise, results obtained are reported as specific rate constants.

As shown in Fig. 6, the Arrhenius plot for butyl oleate supports the above correlation based on the mixture temperature. The activation energies of both homogeneous and heterogeneous catalyzed esterifications result nearly equal, $E_0 \simeq 10.9$ kcal/mole. If the reaction step is occurring only at the external surface of particle (7), a pseudo-chemical regime is controlling and the observed activation energy must be con-

sidered the true activation energy of the heterogeneous catalyzed reaction.

CONCLUDING REMARKS

A retarding effect of water on the process rate has been found by Levesque and Craig (7).

More recently, the deactivation of the resin catalyst by water has been hypothesized by Bochner et al. (8). Water has been assumed forming hydrated ions with the hydrogen counterions of the resin, which become inactive with respect to catalysis of esterification. Alternatively, the decreasing of the distribution coefficient of acid or alcohol by water has been advanced (8), though this occurrence has been considered less likely.

In the previous paper (6) we have reported the behavior of both water concentration and temperature of the reaction mixture. These, after the first steps of reaction assumed with time approximately constant values, dependent on the distillation rate. The higher distillation rate gave at the same time the higher water concentration, the lower reaction temperature, and the lower reaction rate. Therefore, deactivation of catalyst by water might be considered likely.

The results obtained in the present investigation, concerning both homogeneous and heterogeneous catalysis, show, at different boiling pressures, similar behavior of water concentration and reaction temperature with distillation rate. From the Arrhenius plots above presented, where correlations have been based only on the tem-perature of the reaction mixture, we can attribute the effect of the distillation rate on the process rate mainly to the variation of the reaction temperature and the deactivation of catalyst by water, the content of which in the reaction mixture is also dependent on the distillation rate, is not noticeable enough to be demonstrated.

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