Formation and hydrolysis of 4-methoxyphenylacetic acid butyl ester reacting from 4-methoxyphenylacetic acid and *n*-bromobutane using triphase catalysis

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Abstract

The formation and hydrolysis of 4-methoxyphenylacetic acid butyl ester reacting from 4-methoxyphenylacetic acid and *n*-bromobutane using triphase catalysis in a dichloromethane/alkaline solution were investigated. The concentrations of base, reactant and catalyst, water volume, temperature, agitation rate, as well as the kinds of catalysts and salts were evaluated to find the optimum reaction conditions. The formation reaction was a slow reaction and controlled only by chemical kinetics. The hydrolysis reaction was heavily influenced by film diffusion of reactant on the catalyst. The reactive environment in the catalytic pellet plays a crucial role in a triphase reaction, and the effect of KOH is better than that of NaOH. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Reaction kinetics; Ether–ester; Phase-transfer catalysis; Hydrolysis; Triphase catalysis
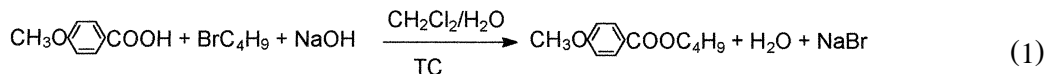
1. Introduction

Liquid–liquid phase-transfer catalysis (LLPTC) is an effective tool for synthesizing organic chemicals from two immiscible reactants [1–3]. However, the process of using a two-phase, phase-transfer catalytic reaction always encounters the problem of separation and purifying the final product from the catalyst. Regen [4] first used a solid-phase catalyst (triphase catalyst, TC), in which the tertiary amine was immobilized on a polymer support, in the reaction between an organic reactant and an aqueous reactant. Thus, filtration or centrifugation can easily separate the insoluble polymer-supported phase-transfer catalyst from the reaction mixtures. The most common methods used for triphase catalysis are reviewed in Regen [4–7], Regen and Besse [8], Tomoi and Ford [9,10] and Tomoi et al. [11–13].

Ether–ester compounds have applications as anticholesteremics, antilipemics, hypocholesteremic agents and hypolipemics for medical compounds [14–17]. Although many methods are known for the preparation of ether–ester compounds [14–20], the synthesis using metal sodium and reflux is intense. You [21] indicated that liquid–liquid phase-transfer catalysis is a useful method for synthesizing

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ether–ester compounds since the reaction condition is mild, and the yield of ether–ester compounds is high. Hence, we use liquid–solid–liquid triphase catalysis to replace liquid–liquid phase-transfer catalysis in order to solve the separation program. Such an analysis has advantages for large-scale applications. The model reaction of synthesizing ether–ester compound used in this study is shown in Eq. (1).

$$CH_3O\text{—}\langle\text{—}\rangle\text{—}COOH + BrC_4H_9 + NaOH \xrightarrow[\text{TC}]{\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}} CH_3O\text{—}\langle\text{—}\rangle\text{—}COOC_4H_9 + H_2O + NaBr \qquad (1)$$

This work reports the kinetics of formation and hydrolysis of 4-methoxyphenylacetic acid butyl ester in a dichloromethane/alkaline solution and discusses the mass-transfer effect of a reactant in the triphase reaction.

2. Experimental section

2.1. Materials

4-Methoxyphenylacetic acid, *n*-bromobutane, and other reagents were reagent grade chemicals.

2.2. Procedures

2.2.1. Preparation of triphase catalyst

The synthetic procedure used for polymer-supported phase-transfer catalyst (triphase catalyst) was identical to that of Meng [22]. The compositions in the resin were: styrene (76 wt.%), chloromethyl styrene (20 wt.%) and divinylbenzene (4 wt.%, cross-linkage). The particle sizes of polymer pellets were determined by sieve analysis. Weight percentages of polymer collected were 20–40 mesh = 16%, 40–80 mesh = 31%, 80–120 mesh = 27%, 120–200 mesh = 19%, 200–400 mesh = 7%.

Twenty grams of polymer pellets, 40 cm^3 of dimethyl formamide, and 60.0 g tri-*n*-butyl amine, was introduced into a 250-cm^3 flask at 60°C. The reaction mixture was agitated (400 rpm) for 6 days. The polymer was then filtered and washed with methanol, acetone and anhydrous methanol, and then dried under vacuum at 60°C. The chloride ion content, as determined by the Volhard method, was 0.71 meq/g.

2.2.2. Synthesis of 4-methoxyphenlyacetic acid butyl ester

An aqueous solution of potassium hydroxide (20 g), water (50 cm^3), 4-methoxyphenylacetic acid (2.9 g), and triphase catalyst (1.5 g) was prepared and introduced into the reactor (250 cm^3, three-necked flask) which was thermostat-controlled to the desired temperature (35 ± 0.02°C). Measured quantities of *n*-bromobutane (5.98 g) and dichloromethane (100 cm^3), also at the desired temperature, were then added to the reactor. The reaction mixture was agitated for 5 h. After reaction, the oil phase, which had separated from the aqueous phase, was washed with water and sodium hydroxide solution several times, and dried with MgSO$_4$. Most of the solvent from the organic phase

was removed by using aspiration. A yellowish oil-like product was subsequently obtained. Finally, the product was separated by vacuum distillation.

2.2.3. Kinetics of the triphase catalytic reaction

For a kinetic run, an aliquot sample was withdrawn from the reaction solution at a selected time interval. The sample (0.2 cm^3) was immediately added to a solution (0.5 cm^3 dichloromethane/0.5 cm^3 of diluted hydrochloric acid) to quench the reaction. The organic phase content was then quantitatively analyzed by HPLC using the method of internal standard. The standard reaction conditions were chosen: (i) for formation reaction: dichloromethane $= 100$ cm^3, *n*-bromobutane $=$ 0.0877 mol, aqueous solution $= 50$ cm^3, $CH_3OC_6H_4COOH = 0.0176$ mol, $KOH = 7$ M, Resin (60–80 mesh, 0.71 meq/g) $= 1.5$ g, 800 rpm, 35°C, and (ii) for hydrolysis reaction: dichloromethane $= 100$ cm^3, $CH_3OC_6H_4COOC_4H_9 = 5.36 \times 10^4$ mol, aqueous solution $= 50$ cm^3, $KOH = 7$ M, Resin (60–80 mesh, 0.71 meq/g) $= 1.5$ g, 800 rpm, 35°C.

Liquid chromatography was carried out in a Shimadzu LC-10AD instrument, using a column packed with Chemcosorb, 5-ODS H C/N. The eluent was $CH_3OH/H_2 = 2/1$, with a flow rate of 1.0 cm^3/min and was monitored at 254 nm (UV detector). Elemental analysis was performed by Perkin-Elmer 2400-CHN. Mass spectra were obtained from a JEOL SX-102A mass spectrometer. Finally, NMR spectra were observed in deuteriated chloroform on a JEOL, 300 MHz FT-NMR spectrometer.

3. Reaction kinetics

3.1. Hydrolysis of 4-methoxyphenylacetic acid butyl ester

The hydrolyzed mechanism of 4-methoxyphenylacetic acid butyl ester in a dichloromethane/KOH aqueous solution via triphase catalysis is expressed as

$$
\text{(2)}
$$

The overbar, $^-$ denotes the characteristics of the species in the organic phase. Resin$^+$ OH$^-$ represents the triphase catalyst for anion of OH$^-$. According to mechanism (2), the hydrolysis of 4-methoxyphenylacetic acid butyl ester has two reaction paths. Hence, the rate expression of hydrolysis can be written as

$$
-r_{CH_3OC_6H_4COOC_4H_9} = \left(-r_{QOH} + -r_{KOH} \right)
$$
$$
= \left(k_{QOH}[\text{Resin}^+OH^-] + k_{KOH}[KOH] \right)\left[\overline{CH_3OC_6H_4COOC_4H_9} \right]^m \tag{3}
$$

A generalized approach to accurately describe the phase-transfer-catalyzed reaction system involves using a pseudo-first-order hypothesis for the catalytic concentration. Hence, Eq. (3) can be rewritten as

$$-r_{CH_3OC_6H_4COOC_4H_9} = k_{h,app} \left[\overline{CH_3OC_6H_4COOC_4H_9} \right]^m \tag{4}$$

and

$$k_{h,app} = k_{QOH}[Resin^+OH^-] + k_{KOH}[KOH] \tag{5}$$

where $k_{h,app}$ is the apparent reaction-rate constant of hydrolysis of 4-methoxyphenylacetic acid butyl ester.

The integral method of analysis always tests a particular rate equation by integrating and comparing the predicted concentration vs. reaction time curve with the experimental concentration vs. reaction time curve. If the fit is unsatisfactory, another rate equation is suggested and tested. Eq. (4) can be integrated by first-order or second-order analysis, and rewritten as

$$-\ln(1 - X_A) = k_{app} \times t; \quad \text{as} \quad m = 1 \tag{6}$$

or

$$\frac{X_A}{C_{A0}(1 - X_A)} = k_{app} \times t; \quad \text{as} \quad m = 2 \tag{7}$$

where $X_A = 1 - C_A/C_{A0}$, and where C_A and C_{A0} represent the concentration of organic reactant at time of reaction and its initial concentration, respectively. The experiment data at various temperatures and the numerical values for Eqs. (6) and (7) at corresponding reaction times are plotted in Fig. 1. Those experimental data fall on a relatively straight line passing through the origin for Eq. (7). The second-order rate equation tested to fit the data is better than the first-order rate equation, particularly
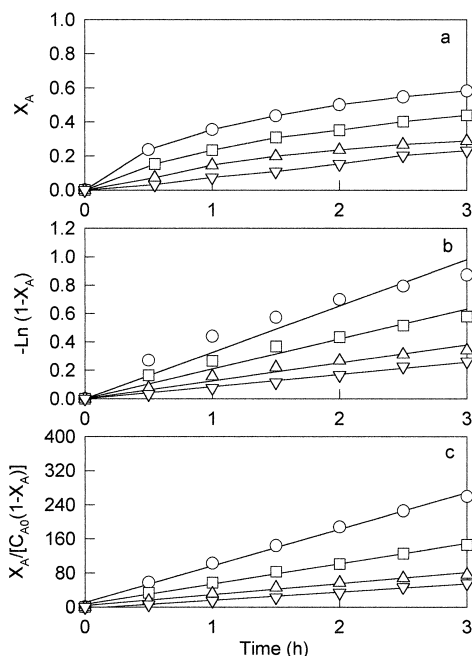
Fig. 1. Test of a rate equation by the integral method of analysis at various reaction temperatures for (a) conversion of 4-methoxyphenoxyacetic acid butyl ester vs. reaction time. (b) using a first-order rate equation of Eq. (6). (c) using a second-order rate equation of Eq. (7). (○): 35°C, (□): 25°C, (△): 15°C, (▽): 5°C.

higher temperatures (or yields). Hence, the apparent second-order reaction was chosen to discuss the hydrolysis reaction in the following sections.

3.2. Formation of 4-methoxyphenylacetic acid butyl ester from 4-methoxyphenylacetic acid and n-bromobutane

The chemical conversion step in which the active catalyst sites (Resin$^+$ with 4-methoxyphenylacetic ions) react with bromobutane in a triphase reaction is expressed as

$$
\begin{array}{c}
H_2O + CH_3O\langle\ \rangle CH_2COOK \xleftarrow{\ (i)\ } KOH + CH_3O\langle\ \rangle CH_2COOH \\[4pt]
+ \qquad\qquad\qquad + \\[2pt]
\rightarrow Resin^+\ Br^- \\
Resin^+ CH_3O\langle\ \rangle CH_2COO^- + C_4H_9OH \\
Resin^+Br^- \qquad (v)\ \\
Resin^+\ OH^- \\
(ii)\qquad\qquad + \qquad (or\ KOH)\ (iv) \\
\overline{BrC_4H_9} + Resin^+CH_3O\langle\ \rangle CH_2COO^- \xrightarrow{\ (iii)\ } Resin^+ Br^- + CH_3O\langle\ \rangle CH_2COOC_4H_9 \\
+ \\
KBr \\
\end{array}
\qquad (8)
$$
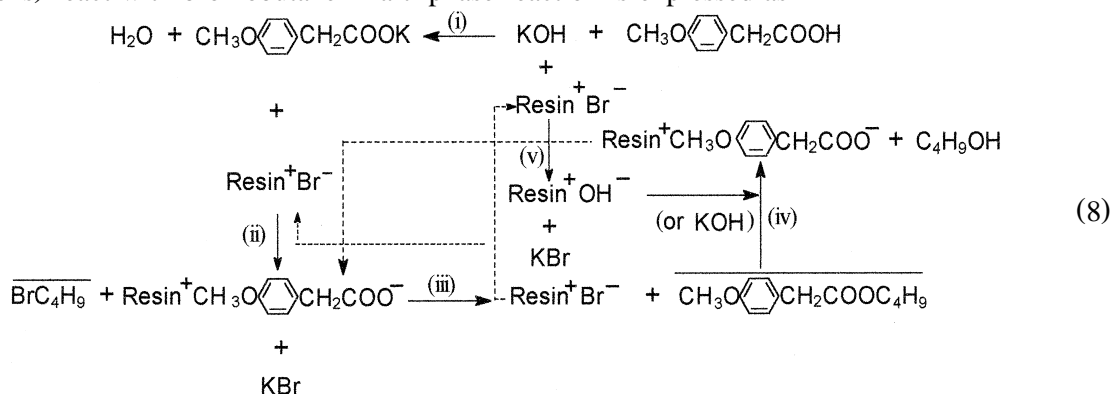
The total moles of catalyst sites thus are

$$\text{Resin}_T = \text{Resin}^+CH_3OC_6H_4COO^- + \text{Resin}^+Br^- \qquad (9)$$

In this study, the reaction rate for the organic phase follows pseudo-first-order kinetics and can be written as

$$
\begin{aligned}
-r_{BrC_4H_9} &= r_{CH_3OC_6H_4COOC_4H_9} \\
&= k_{BrC_4H_9}\left[\text{Resin}^+CH_3OC_6H_4COO^-\right]\left[\overline{BrC_4H_9}\right] \\
&= k_{f,app}\left[\overline{BrC_4H_9}\right]
\end{aligned}
\qquad (10)
$$

where $k_{f,app}$ is the apparent reaction-rate constant for formation of 4-methoxyphenylacetic acid butyl ester. For all the reported values of pseudo-first-order kinetics (Eq. (10)) can be applied up to 90% production of product, depending on reaction conditions. On the basis of experimental results ($k_{h,app}$ and $k_{f,app}$), the reactivity of formation and hydrolysis of 4-methoxyphenylacetic acid butyl ester are analyzed.

4. Results and discussion

The formation of 4-methoxyphenylacetic acid butyl ester (main product) reacting from 4-methoxyphenylacetic acid and n-bromobutane using triphase catalysis is shown in Eq. (8). However, the yield of 4-methoxyphenylacetic acid butyl ester is influenced when the alkaline aqueous solution exists in the reaction system, which stimulates 4-methoxyphenylacetic acid butyl ester to hydrolyze. Hence, the formation and hydrolysis of 4-methoxyphenylacetic acid butyl ester were simultaneously discussed in this study.

Fig. 2 plots the apparent reaction-rate constants $k_{f,app}$ and $k_{h,app}$ vs. the agitation rate and the particle size of triphase catalyst in the formation and the hydrolysis reactions, respectively. $k_{f,app}$
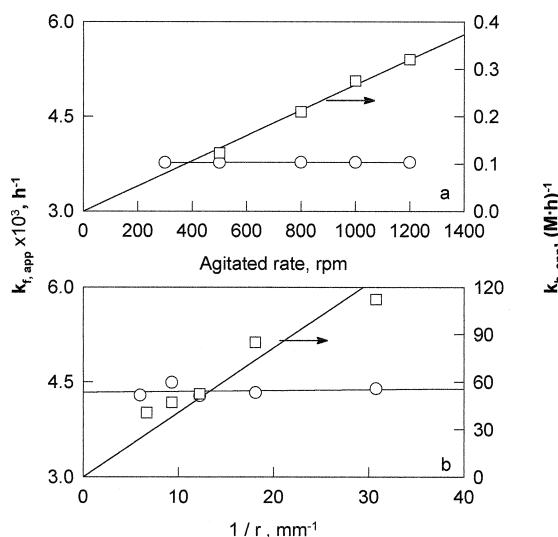
Fig. 2. Effect of apparent reaction-rate constant on (a) agitation rate and (b) particle size.

values are nearly independent of the agitation rate and particle size. This finding demonstrates that the mass-transfer effect does not influence the formation reaction. In addition, the amount of $k_{h,app}$ values is proportional to the agitation rate and reciprocally to the particle size. Hence, the hydrolysis reaction is strongly influenced by film diffusion of 4-methoxyphenylacetic acid butyl ester from bulk solution to catalytic particle.

The temperature effect on the apparent reaction-rate constant is shown in Fig. 3. The results show that the apparent reaction-rate constant increases as the temperature rises. The apparent activation energies of Arrhenius law for the formation and the hydrolysis reactions are 17 and 4.4 kcal/mol, respectively. This result also illustrates that film diffusion of 4-methoxyphenylacetic acid butyl ester controls the hydrolysis reaction because the apparent activation energy for film diffusion is clearer rather than that for chemical reaction (usually 2 to 5 kcal/mol).

Fig. 4 shows the effect of different amounts of triphase catalyst on the apparent reaction-rate constant. The increasing quantity of the catalyst obviously enhances the reaction rate, and the
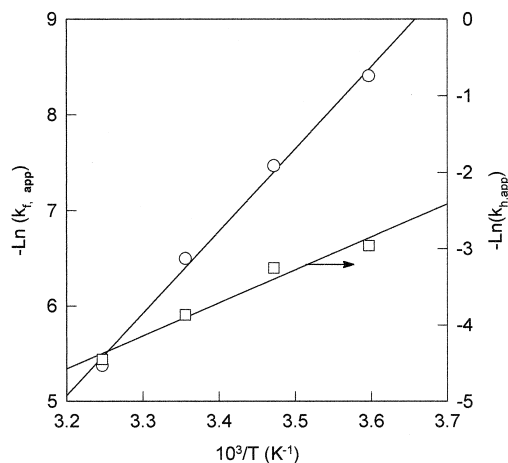
Fig. 3. Effect of apparent reaction-rate constants on various reaction temperatures.
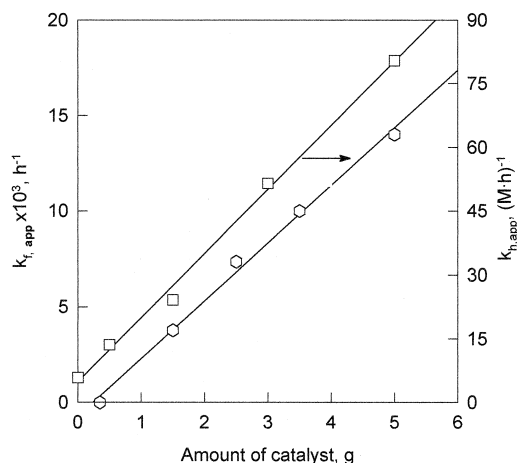
Fig. 4. Effect of apparent reaction-rate constant on amount of triphase catalyst.

apparent reaction-rate constant is proportional with the amount of catalyst. This finding corresponds to Eqs. (3) and (10), and the triphase catalyst reaction is of first order. According to Eq. (5), the $k_{h,app}$ value of the hydrolysis reaction for KOH was 4.95 $(Mh)^{-1}$ in the absence of triphase catalyst. However, because a small amount of triphase catalyst was taken out the solution by attaching to the reactor wall during the course of the reaction, the straight line for $k_{f,app}$ cannot pass through the origin in the formation reaction.

Fig. 5 shows the relationships between $k_{h,app}$, the water volume, and the concentration of 4-methoxyphenylacetic acid butyl ester. The increase of water volume correlated with a slight increase in the $k_{h,app}$ value. Experimental data from previous research [23,24] indicated that decreasing the concentration of organic reactant increased the pseudo-first-order reaction-rate constant. Such an effect is not reasonably explained according to a conventional kinetics model, in which the reaction-rate constant is independent of the concentration of the reactant. The contradiction
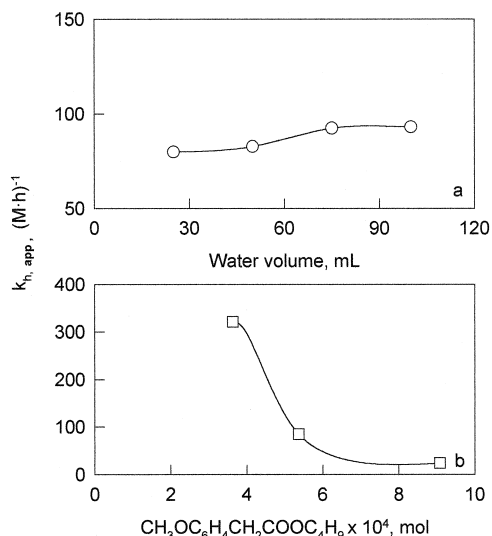
Fig. 5. Effect of apparent reaction-rate constant on (a) water volume and (b) amount of 4-methoxyphenoxyacetic acid butyl ester in the hydrolysis reaction.

between the simulation results of Wu [25] and the experimental results in the above referenced research [23,24] suggests that the apparent reaction-rate constant vary when the concentration of reactant is changed. In addition, it indicated that the mass-transfer rate influences the reaction rate. According to Fig. 5b, the $k_{h,app}$ values strongly depend on the concentration of 4-methoxypheny-lacetic acid butyl ester. The hydrolysis reaction is obviously controlled both by chemical kinetics and mass transfer.

Fig. 6 depicts the relationships between $k_{f,app}$, the water volume, and the concentration of 4-methoxyphenylacetic acid. The $k_{f,app}$ values are independent of both the water volume and the concentration of 4-methoxyphenylacetic acid. The results reveal that mass transfer does not influence the formation reaction. This reaction is a slow reaction, and is only controlled by chemical kinetics. Hence, if all active sites in the catalytic particle could provide effective conduction, the intrinsic reaction-rate constant for the formation reaction should be equal to 0.61 $(Mh)^{-1}$ ($= 4.4 \times 10^{-3} \times 100$ ml/0.71 meq/g).

The four functions of base in a liquid–liquid phase-transfer catalyzed reaction were reported in our previous work [22,26]: (i) reactant; (ii) deprotonation of acidic organic compound to become the reactive form; (iii) salting out the intermediate product of catalyst to the organic phase; or (iv) reducing the solvation of catalyst and water to upgrade the reactivity of active catalyst in the organic phase. In a liquid–solid–liquid triphase reaction, part (iii) is replaced with functions improving the reactive environment in the catalytic pellets, such as swelling volume, imbibed solvent ratio (oil/water), solubility between two phases, etc. Fig. 7 summarizes the effect of base concentration on the apparent reaction-rate constant. The apparent reaction-rate constants were increased with an increasing base concentration in both reactions. Irrespective of whether the base was KOH or NaOH, the reaction phenomenon is similar, and the $k_{h,app}$ values for the two cases were the same in the hydrolysis reaction. The role of base is both as reactant and catalyst, but the reactivity of organic reactant, 4-methoxyphenylacetic acid butyl ester, is not influenced. In the formation reaction, $k_{f,app}$ values in the KOH solution were larger than those in the NaOH solution. Meng [22] reported that the capability of NaOH for reducing the solvation between catalyst and water to upgrade the reactivity of
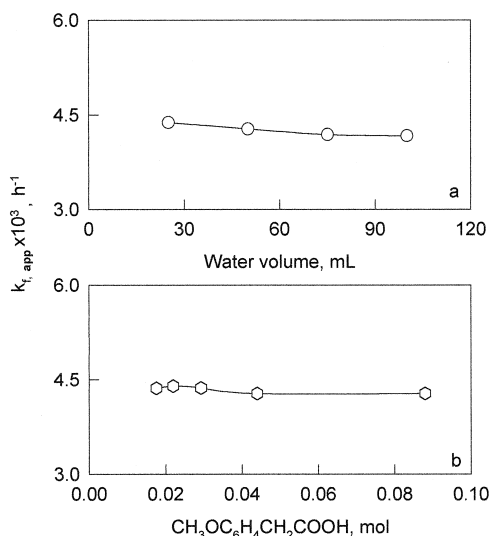

Fig. 6. Effect of apparent reaction-rate constant on (a) water volume and (b) amount of 4-methoxyphenoxyacetic acid in the formation reaction.
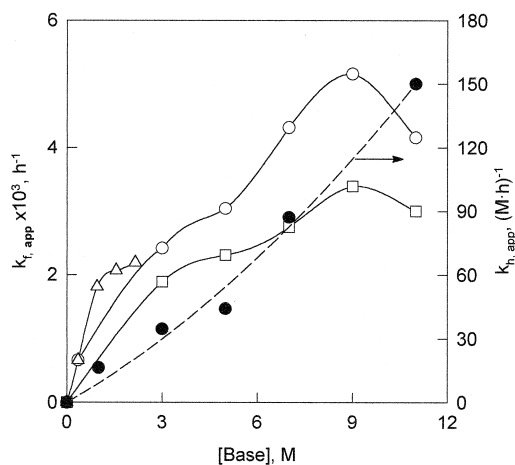
Fig. 7. Effect of apparent reaction-rate constant on base concentration for ($\bigcirc$): KOH, ($\square$) NaOH, ($\triangle$) KOH (0.0176 M) + K_2CO_3, ($\bullet$): KOH.

active catalyst is larger than that for KOH. That is, the intrinsic reaction-rate constant of NaOH is larger than that of KOH under the same reaction conditions. However, the experimental results shown in Fig. 7 indicate the contrary. Fig. 8 shows the imbibed solvent composition in the catalytic pellet. The procedure for determining imbibed solvent composition of the catalyst is identical to that of Wang and Wu's report [27]. The amounts of H_2O and CH_2Cl_2 for KOH are larger than the corresponding amounts for NaOH. That is, the reactive environment in the catalytic pellet for KOH is better than that of NaOH. Hence, we clarify that the reactive environment in the catalytic pellet plays a crucial role in a triphase reaction.

Five reactions were shown in mechanism (8). Reaction (iv) is the hydrolysis reaction of 4-methoxyphenylacetic acid butyl ester. From experimental data, the reaction rate for hydrolysis reaction exceeds by 10 times the rate for formation reaction. However, the sequence of the association capability between $Resin^+$ and anion is $CH_3OC_6H_4CH_2COO^- > Br^- > OH^-$. The concentration of $Resin^+OH^-$ is rare in the formation reaction. The hydrolyzed reaction rate is small, depending only
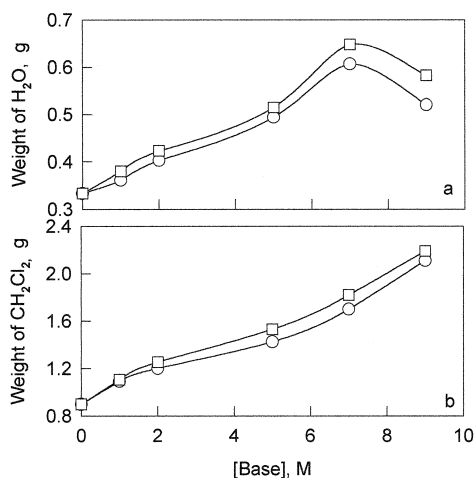

Fig. 8. Effect of base concentration on imbibed solvent composition in the catalytic pellet: resin = 1 g, H_2O = 25 cm^3, CH_2Cl_2 = 25 cm^3, 25°C ($\bigcirc$): NaOH, ($\square$) KOH.

on the concentration of KOH in mechanism (8). Hence, the $k_{f,app}$ value increased with an increasing base concentration.

However, when the KOH (or NaOH) concentration increases, the hydrolyzed reaction rate increases. According to mechanism (8) under this condition, the formation of 4-methoxyphenylacetic acid butyl ester is impeded. When other salts (K_2CO_3, NaCl and KBr) were supplemented into the reaction system to test the effect of salt, $k_{h,app}$ values observed for no salt added, 0.1 mol K_2CO_3, 0.1 mol NaCl, and 0.1 mol KBr were 23.0, 18.1, 11.3 and 10.2 $(Mh)^{-1}$, respectively. The $Resin^+OH^-$ concentration is reduced because the salt anion ($^=CO_3$, ^-Cl or ^-Br) competes with the hydroxide ion for the active site in the resin, thus decreasing the hydrolyzed reaction rate. If the reaction condition was chosen in the formation reaction as follows: dichloromethane = 100 cm^3, *n*-bromobutane = 0.0877 mol, aqueous solution = 50 cm^3, $CH_3OC_6H_4COOH$ = 0.0176 mol, KOH = 0.0176 mol, Resin (60–80 mesh, 0.71 meq/g) = 1.5 g, 800 rpm, 35°C, and K_2CO_3 supplemented, then the $k_{f,app}$ value increased with an increasing concentration of K_2CO_3 (Fig. 7). Because the K_2CO_3 supplement could not alter the imbibed solvent composition in the resin, the $k_{f,app}$ value slightly increased when the concentration of K_2CO_3 extra-added exceeded 1 M. Hence, the enhancing effect for reactivity is limited.

Fig. 9 shows the effectiveness relationship between liquid–liquid phase-transfer catalyst (*n*-(C_4H_9)NBr) and triphase catalyst in the present study for equal mole quantity. The reaction rate of biphase catalyst gradually increased over that of triphase catalyst when the reaction time increased. This result illustrates that the mass transfer of reactant can be neglected in a liquid–liquid phase-transfer-catalyzed reaction, although in a triphase reaction the mass transfer influences the overall reaction rate. Hence, larger amounts of triphase catalyst added to the reaction system are needed. When the particle size of triphase catalyst used in reaction system reduced from 220 μm (60–80 mesh) to below 75 μm (200-mesh) and the mole ratio of triphase catalyst to biphase catalyst exceeds 3, the triphase reaction rate can compete the biphase reaction rate. The yield of 4-methoxyphenylacetic acid butyl ester exceeded 98% as the reaction time is less than 3 h.

The function group of triphase catalyst in this study is $Resin-CH_2N(C_4H_9)_3^+Cl^-$. When the commercial ion-exchange resins (Amberlite: IRA-900, IRA-904, A26, A27; Dowex 1×2 for $Resin-CH_2N(CH_3)_3^+Cl^-$, and Amberlite IRA-410 for $Resin-CH_2N(CH_3)_2(C_2H_4OH)^+Cl^-$, and Am-
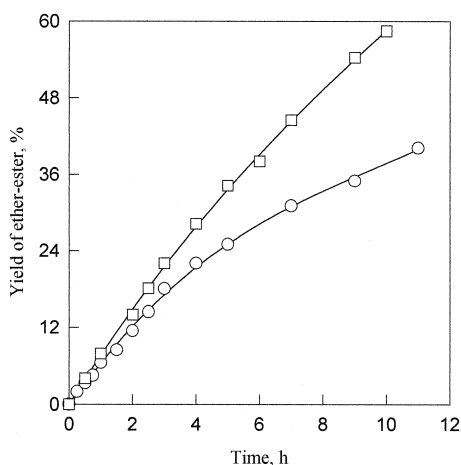

Fig. 9. Plot of yield of 4-methoxyphenoxyacetic acid butyl ester on reaction time in the formation reaction for 3×10^{-3} mol of (○): triphase catalyst in this study and (□): (*n*-C_4H_9)NBr.

berlite IRA-410 for Resin-$CH_2N(CH_3)_2(C_2H_4OH)^+Cl^-$) were employed as triphase catalyst, no product was observed after 6 h of reaction time, indicating that these kinds of catalysts are too hydrophilic to develop a good reactivity environment.

5. Conclusion

The kinetics of formation and hydrolysis of 4-methoxyphenylacetic acid butyl ester reacting from 4-mehoxyphenylacetic acid and *n*-bromobutane using triphase catalysis in a dichloromethane/alkaline solution were investigated. Although the hydrolyzed reaction rate of 4-methoxyphenylacetic acid butyl ester is rapid, a higher yield of 4-methoxyphenylacetic acid butyl ester was obtained in the formation reaction by triphase catalysis. The reactive environment in the catalytic pellet (such as swelling volume, imbibed solvent ratio (oil/water), solubility between two phases, and concentrations of reactant and salt) plays a crucial role in improving the triphase reaction rate.

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