Oxidation of Benzyl Alcohol Using Hypochlorite Ion Via Phase-Transfer Catalysis

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Heterogeneous oxidation of benzyl alcohol using hypochlorite ion with phase-transfer catalyst is carried out in an agitated vessel with a flat interface. Cetyltrimethylammonium bromide and toluene are chosen as the best catalyst and solvent, respectively. Observed reaction rates are proportional to the interfacial concentration of cetyltrimethylammonium hypochlorite in the organic phase, which is formed by ion exchange between bromide and hypochlorite ions. They are reasonably explained by the proposed theoretical model for the phase-transfer catalysis. The reaction rate constant evaluated by fitting the rate data to the model prediction is 22.7 $m^3/kmol \cdot s$ at 303 K, independent of the physical properties in the aqueous solutions. The maximum yield of benzaldehyde is about 90% and the selectivity is 100% for the conversion of hypochlorite ion less than 80%.

Introduction

For the oxidation of organic compounds, many inorganic oxidants, such as permanganate, chromate, and hypochlorite are frequently used. However, since the mutual solubilities of the organic compounds and the inorganic oxidants in the heterogeneous liquids systems are usually very small, the reactivity of the reactants in the organic and aqueous phases is low. The use of a phase-transfer catalyst can overcome this difficulty. It has been reported that many inorganic oxidants can be transferred into the organic phase using phase-transfer catalysis (Starks and Liotta, 1978; Dehmlow and Dehmlow, 1983). Thus, a phase-transfer catalyst can enhance the rate of heterogeneous reaction between mutually insoluble organic and aqueous phases at rather mild conditions by shuttling the reactant.

Since Lee and Freedman (1976) have demonstrated that hypochlorite ion can be transferred into an organic phase by using quaternary ammonium salts for the oxidation of alcohols and amines, the oxidation of alcohol by hypochlorite ion in the presence of phase-transfer catalyst has been reported by several investigators (Krishnan et al., 1977; Tabushi and Koga, 1979; Do and Chou, 1990). However, in these studies the main reaction in the organic phase was claimed to be rate-determining, because the reaction rates for the evaluated system was slow, or the experiment was carried out under conditions in which the mass-transfer resistance of relevant species might be made negligible by high stirring. Thus, an approach for conditions in which the mass-transfer resistance of relevant species is not negligible has rarely been achieved. In a previous article, we carried out the alkaline hydrolysis of *n*-butyl acetate by using a phase-transfer catalyst, and discussed a reasonable analytical procedure of the overall reaction rate for phase-transfer catalysis (Asai et al., 1992).

In the present work, we analyzed the oxidation of benzyl alcohol by using hypochlorite ion via phase-transfer catalysis. The product benzaldehyde is an important starting reactant for the manufacture of certain odorants, various dyes and chemicals, such as flavor, perfume, and soap. At present, benzaldehyde has been producing by the direct oxidation of toluene, or by the side-chain chlorination of toluene by hydrolysis of benzal chloride. However, in these processes, operation at a high temperature is required and a low yield due to the formation of the byproducts has been pointed out in industrial operations. The use of a phase-transfer catalyst can overcome these disadvantages.

In this work, the effects of various kinds of phase-transfer catalysts and solvents on the overall reaction rates for the oxidation of benzyl alcohol were first investigated in heterogeneous liquid-liquid reaction systems. Next, the overall reaction rates were measured by varying the concentrations of the chosen catalyst and hypochlorite ion, and the reaction rate constant was evaluated by comparing them with a theoretical

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Table 1. Effect of Phase-Transfer Catalyst and Solvent on Overall Reaction Rates

PTC	Solvent	Overall Reaction Rate (kmol/m^2·s)
CTMAC	toluene	7.45×10^{-7}
CTMAB	toluene	1.02×10^{-6}
TBAB	toluene	5.87×10^{-8}
TBPB	toluene	1.04×10^{-7}
TOMAC	toluene	6.71×10^{-8}
CTMAB	benzene	8.36×10^{-7}
CTMAB	1,2-dichloroethane	1.78×10^{-7}
CTMAB	chloroform	4.33×10^{-7}

Temperature = 303 K; organic phase: $[\overline{C_6H_5CH_2OH}]_0 = 0.926$ kmol/m^3; aqueous phase: $[PTC]_0 = 0.01$ kmol/m^3; $[OCl^-]_0 = 0.1$ kmol/m^3.

solution considering the mass-transfer resistance of relevant reaction species.

Experimental

To begin with, the effects of various kinds of solvents and catalysts on the overall reaction rate for the oxidation of benzyl alcohol were examined. The organic solvents used were benzene, toluene, 1,2-dichloroethane, and chloroform, and the phase-transfer catalysts were cetyltrimethylammonium chloride (CTMAC), cetyltrimethylammonium bromide (CTMAB), tetrabutylammonium bromide (TBAB), tetrabutylphosphonium bromide (TBPB), and trioctylmethylammonium chloride (TOMAC). The experimental apparatus used in this study was an agitated vessel with a flat interface, similar to that used in a previous work (Asai et al., 1983). Both the organic and aqueous phases had equal volumes. The experiments were carried out at 303 K and at agitation speeds of 0.83 1/s for each phase by using an organic phase of 0.926 kmol/m^3 benzyl alcohol diluted by each organic solvent and an aqueous phase containing 0.1 kmol/m^3 hypochlorite ion OCl^- and 0.01 kmol/m^3 catalyst. The hypochlorite ion in the aqueous phase was prepared by dissolving high chlorinated lime in water and then filtering it off, and its concentration was determined by iodometry. Furthermore, the pH of the aqueous phase was adjusted to the range of 8.0–9.0 by the addition of aqueous HCl solution. The overall reaction rates for each system were evaluated from the decrease in the aqueous phase concentration of OCl^- ion with time, as listed in Table 1. This reaction did not substantially occur for the noncatalyst system under ordinary pressure and temperatures, but the overall reaction rates were accelerated by the addition of any phase-transfer catalyst under mild conditions. From these results as the optimum catalyst and solvent, CTMAB and toluene, respectively, were chosen and used in the subsequent main experiments.

In the main experiments, the upper organic phase was 0.194–1.94 kmol/m^3 benzyl alcohol diluted with toluene. The lower aqueous phase consisted of the solutions containing 0.025–0.5 kmol/m^3 OCl^- ion and 0.002–0.02 kmol/m^3 CTMAB. Samples of $1.0\times10^{-6}-2.0\times10^{-6}$ m^3 were taken from the aqueous and organic phases, respectively, at intervals of 10 min. The total concentration of bromide ion Br^- and chloride ion Cl^- in the aqueous phase was measured by the Mohr method or mercury (II) thiocyanate method with an ultraviolet spectrophotometer. The concentrations of benzaldehyde and benzoic acid in the organic phase were measured by high performance liquid chromatography.

The overall reaction rates were evaluated from the concentration variations of OCl^- ion or benzaldehyde with time. The experiments were carried out at agitation speeds of 0.83 1/s for each phase and the temperature of 303 K.

Reaction Model and Analytical Procedure

The reaction model for the present phase-transfer catalyzed reaction system is shown in Figure 1. CTMAB (Q^+Br^-), which substantially exists in the aqueous phase, dissociates into two ions, Q^+ and Br^-, according to reaction b. The dissociated Q^+ reacts with OCl^- existing originally in the aqueous phase to form the ion pair Q^+OCl^- (reaction c). The formed Q^+OCl^- moves to the organic phase and reacts with $C_6H_5CH_2OH$, which already exists there (reaction a). The main reaction a can be regarded as a pseudo first-order reaction with respect to Q^+OCl^-, because $[\overline{C_6H_5CH_2OH}] \gg [Q^+OCl^-]$. The resulting ion pair Q^+Cl^- transfers to the aqueous phase and dissociates partially into Q^+ and Cl^- (reaction d). The dissociated ion Q^+

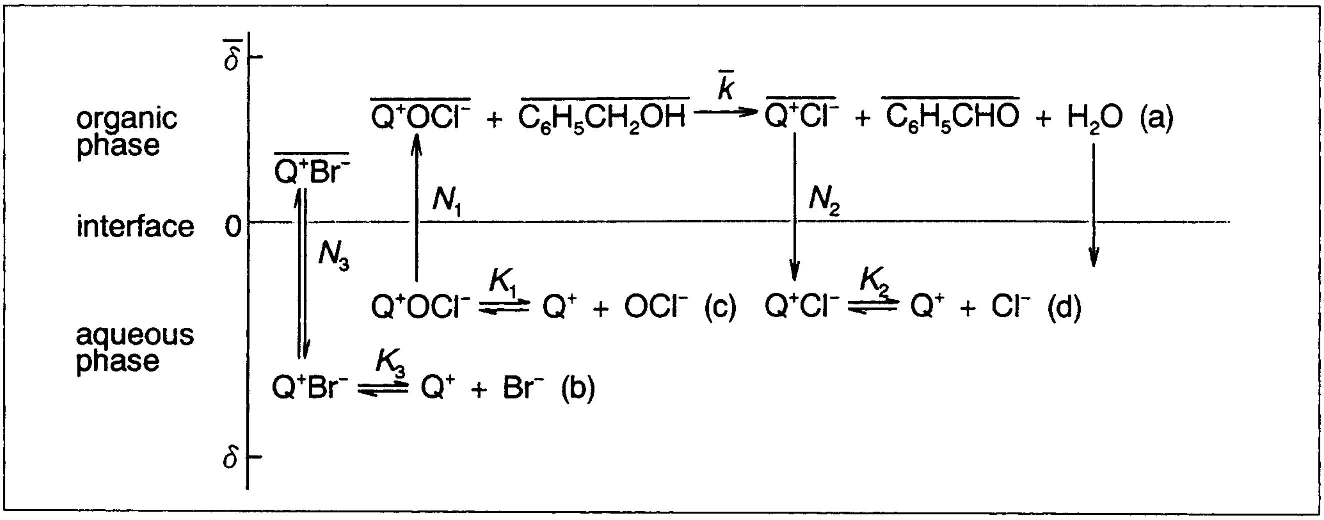

Figure 1. Reaction model.

contributes to the formation of Q^+OCl^- again, and this catalytic reaction cycle is repeated. The dissociations of Q^+X^- ($X^- = OCl^-, Cl^-, Br^-$), according to reactions b-d, may be regarded as an instantaneous reversible reaction, similar to tricaprylmethylammonium chloride (Aliquat 336) (Asai et al., 1991).

The differential equations, based on the film theory for the relevant species in the organic phase, can be expressed as:

$$\overline{D}_j \frac{d^2[\bar{j}]}{dz^2} = \overline{R}_j \quad (j = Q^+OCl^-, C_6H_5CH_2OH) \tag{1}$$

$$\overline{D}_j \frac{d^2[\bar{j}]}{dz^2} = -\overline{R}_j \quad (j = Q^+Cl^-) \tag{2}$$

where

$$\overline{R}_j = \bar{k}\,[\overline{C_6H_5CH_2OH}]_b[\overline{Q^+OCl^-}] = \bar{k}'\,[\overline{Q^+OCl^-}] \tag{3}$$

On the other hand, for the species in the aqueous phase, the diffusion equations can be expressed as:

$$D_j \frac{d^2[j]}{dz^2} = R_j \quad (j = Q^+OCl^-, Q^+Cl^-, Q^+Br^-) \tag{4}$$

$$D_j \frac{d^2[j]}{dz^2} = -R_j \quad (j = Q^+, OCl^-, Cl^-, Br^-) \tag{5}$$

where R_j = net consumption rate of species j by reactions b-d.

The boundary conditions for these equations are:

$$\begin{aligned}
z = \bar{\delta};\ & [\bar{j}] = [\bar{j}]_b && (j = Q^+Cl^-, C_6H_5CH_2OH)\\
& [\overline{Q^+OCl^-}] = 0 &&\\
z = 0;\ & [\bar{j}] = [\bar{j}]_i && (j = Q^+OCl^-, Q^+Cl^-, C_6H_5CH_2OH)\\
& [j] = [j]_i && (j = \text{all species existing in the aqueous phase})\\
z = \delta;\ & [j] = [j]_b && (j = \text{all species existing in the aqueous phase})
\end{aligned} \tag{6}$$

Mass balances of all species existing in the aqueous phase at the interface ($z = 0$) result in:

$$N_j = -\overline{D}_j \frac{d[\bar{j}]}{dz}\bigg|_{z=0} = -D_j \frac{d[j]}{dz}\bigg|_{z=0} + r_j \tag{7}$$

where r_j is the consumption rate of species j at the interface, according to reactions b-d.

From the distribution equilibria of Q^+X^- ($X^- = OCl^-, Cl^-, Br^-$):

$$[Q^+X^-]_i = m_{Q^+X^-}[\overline{Q^+X^-}]_i \tag{8}$$

The dissociation equilibria of Q^+X^- ($X^- = OCl^-, Cl^-, Br^-$) may be expected to hold at any place in the aqueous phase:

$$K_{Q^+X^-} = \frac{[Q^+]_i[X^-]_i}{[Q^+X^-]_i} = \frac{[Q^+]_b[X^-]_b}{[Q^+X^-]_b} \tag{9}$$

From the mass balance of the relevant species in both phases having the equal volumes:

$$[OCl^-]_{obs} = [Q^+OCl^-]_b + [OCl^-]_b \tag{10}$$

$$([Cl^-] + [Br^-])_{obs} = [Q^+Cl^-]_b + [Cl^-]_b + [Q^+Br^-]_b + [Br^-]_b \tag{11}$$

$$[Q^+Br^-]_0 = [\overline{Q^+Br^-}]_b + [Q^+Br^-]_b + [Br^-]_b \tag{12}$$

$$[OCl^-]_0 + [Cl^-]_0 = [Q^+OCl^-]_b + [OCl^-]_b + [\overline{Q^+Cl^-}]_b + [Q^+Cl^-]_b + [Cl^-]_b \tag{13}$$

$$[Q^+]_0 = [Q^+OCl^-]_b + [Q^+Cl^-]_b + [Q^+Br^-]_b + [Q^+]_b + [\overline{Q^+Cl^-}]_b + [\overline{Q^+Br^-}]_b \tag{14}$$

As will be shown later, mass transfer of Q^+Br^- from the aqueous phase to the organic phase may be considered to be negligible from the consideration of the distribution and dissociation equilibria of Q^+Br^-. Moreover, judging from the dissociation equilibrium of Q^+X^- ($X^- = OCl^-, Cl^-, Br^-$) ion pairs in the aqueous phase, the aqueous phase concentration of Br^- may be seen to be considerably higher than that of Q^+. Thus, the following approximate relations hold:

$$[\overline{Q^+Br^-}]_b \simeq 0 \tag{15}$$

$$[Q^+Br^-]_i \simeq [Q^+Br^-]_b \tag{16}$$

$$[Br^-]_i \simeq [Br^-]_b \tag{17}$$

Solving Eqs. 1-10, 16 and 17, one obtains the following expressions for the overall reaction rate, that is, the mass-transfer rate N_1 of Q^+OCl^- across the interface and for the interfacial concentration of Q^+OCl^- in the organic phase:

$$N_1 = \frac{\bar{\gamma}}{\tanh \bar{\gamma}}\, \bar{k}_{L1}[\overline{Q^+OCl^-}]_i \tag{18}$$

$$[\overline{Q^+OCl^-}]_i = \frac{\dfrac{[OCl^-]_{obs}[Q^+]_b}{m_1([Q^+]_b + K_1)} \left(\dfrac{k_{L1}}{k_{L5}}[Q^+]_b + K_1\right)}{K_1 - \dfrac{[Q^+]_b}{m_1 k_{L5}} \left(\dfrac{\bar{\gamma}}{\tanh \bar{\gamma}}\, \bar{k}_{L1} - m_1 k_{L1}\right)} \tag{19}$$

where

$$\bar{\gamma} = \sqrt{\bar{k}\,\overline{D}_1[\overline{C_6H_5CH_2OH}]_b}/\bar{k}_{L1},\quad \bar{k}_{Lj} = \overline{D}_j/\bar{\delta},\quad k_{Lj} = D_j/\delta \tag{20}$$

The value of $\bar{\gamma}$ can be evaluated by comparing the observed mass-transfer rates N_1 with Eqs. 18 and 19, using $[Q^+]_b$ calculated from Eqs. 9-15. Thus, one can determine the reaction rate constant $\bar{k}$ from the evaluated value of $\bar{\gamma}$ by means of Eq. 20.

Physical Properties

The densities, the viscosities, and the interfacial tensions of the solutions used in all the experiments were measured in a similar manner to those in a previous article (Asai et al., 1992). The diffusivity of Q^+Br^- in the organic phase was measured using a conventional diaphragm cell.

The distribution and dissociation equilibria of Q^+Cl^- and Q^+Br^- were measured at 303 K for the toluene-aqueous electrolyte solution systems, according to the previous procedure (Asai et al., 1993). The effect of existence of benzyl alcohol was not appreciable. The distribution and dissociation equilibria of Q^+OCl^- were evaluated indirectly using the Q^+Cl^--toluene-$Ca(OCl)_2$ solution system, since Q^+OCl^- of reagent grade was not available. Consequently, the following relations were obtained for the distribution coefficients $m_{Q^+X^-}$ and the dissociation constants $K_{Q^+X^-}$ ($X^- = OCl^-, Cl^-, Br^-$).

$$\log(m_1/6.70) = -(0.766I_{Ca(OCl)_2} + 0.790I_{CaCl_2} + 0.781I_{CaBr_2}) \quad (21)$$

$$K_1 = 8.64 \times 10^{-4}\ \text{kmol/m}^3 \quad (22)$$

$$\log(m_2/3.38) = -(0.301I_{Ca(OCl)_2} + 0.325I_{CaCl_2} + 0.316I_{CaBr_2}) \quad (23)$$

$$K_2 = 6.65 \times 10^{-3}\ \text{kmol/m}^3 \quad (24)$$

$$\log(m_3/2.14) = -(0.312I_{Ca(OCl)_2} + 0.336I_{CaCl_2} + 0.327I_{CaBr_2}) \quad (25)$$

$$K_3 = 4.25 \times 10^{-3}\ \text{kmol/m}^3 \quad (26)$$

These results reveal that Q^+Br^- ion pairs substantially exist in the aqueous phase and dissociate almost completely into ions Q^+ and Br^-, because the dissociated Q^+ ion is consumed by the reaction with OCl^- ion.

The diffusivity of Q^+OCl^- in the organic phase at 303 K was predicted from the observed organic phase diffusivity of $Q^+Br^- = 3.13 \times 10^{-9}$ m²/s, according to a previous procedure (Asai et al., 1991) and was found to be 2.81×10^{-9} m²/s. The diffusivities D_{jw} of Q^+OCl^-, Q^+Cl^-, and Q^+Br^- in water were predicted to be 8.02×10^{-10} m²/s, 8.91×10^{-10} m²/s, and 8.96×10^{-10} m²/s, respectively, at 303 K by using the Nernst-Planck equation in line with the previous work (Asai et al., 1991). The diffusivities of cetyltrimethylammonium salts, Q^+OCl^-, Q^+Cl^-, and Q^+Br^- in the aqueous mixed electrolyte solutions for the reactive systems were predicted from the following equation on the basis of the correlation of Hikita et al. (1979):

$$D_j/D_{jw} = 1 - 0.194[Ca(OCl)_2] + 0.172[CaBr_2] + 0.154[CaCl_2] \quad (j = Q^+OCl^-, Q^+Cl^-, Q^+Br^-) \quad (27)$$

The diffusivities of OCl^-, Cl^-, and Br^- ions in the aqueous electrolyte solutions were estimated from the Vinograd-McBain equation (1948).

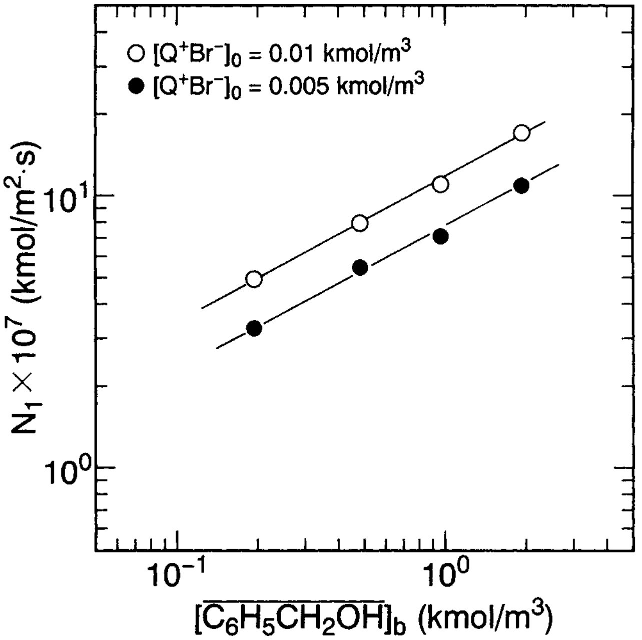

Figure 2. Effect of bulk concentration of $C_6H_5CH_2OH$ in organic phase on overall reaction rates at 303 K and 0.1 kmol/m³ OCl^- ion in aqueous phase.

The mass-transfer coefficients $\bar{k}_{Lj}$ and k_{Lj} of relevant species in the organic and aqueous phases, respectively, were predicted from the empirical correlation of Asai et al. (1983).

Results and Discussion

Figure 2 illustrates the effect of the bulk concentration of $C_6H_5CH_2OH$ in the organic phase on the overall reaction rates N_1 of Q^+OCl^- at 0.005 and 0.01 kmol/m³ CTMAB (Q^+Br^-). The overall reaction rates, that is, the mass-transfer rates N_1 increase with the bulk concentration of $C_6H_5CH_2OH$. The data points for each concentration of Q^+Br^- can be correlated by the straight line with the slope equal to 0.5. When the main reaction a in the organic phase occurs in the fast pseudo first-order reaction regime, that is, $\bar{\gamma} > 3$, Eqs. 18 and 20 can be written as:

$$N_1/\sqrt{\bar{D}_1[\overline{C_6H_5CH_2OH}]_b} = \sqrt{\bar{k}}[\overline{Q^+OCl^-}]_i \quad (28)$$

Thus, Figure 2 confirms that this reaction system is of first-order with respect to the bulk concentration of $C_6H_5CH_2OH$ in the organic phase.

Figure 3 shows the effect of the bulk concentration of Q^+Br^- in the aqueous phase on the overall reaction rates N_1 with the parameter of the initial $C_6H_5CH_2OH$ concentration. The overall reaction rates N_1 may be seen to increase in proportion to the bulk concentration of Q^+Br^-.

Figure 4 represents mass-transfer rates N_1, which are plotted against the bulk concentration of OCl^- ion in the aqueous phase for the two initial concentrations of Q^+Br^-. The overall reaction rates N_1 for each Q^+Br^- concentration may be seen to increase with the bulk concentration of OCl^- ion.

The lefthand side of Eq. 28 should be proportional to the interfacial concentration $[\overline{Q^+OCl^-}]_i$ of Q^+OCl^- in the organic

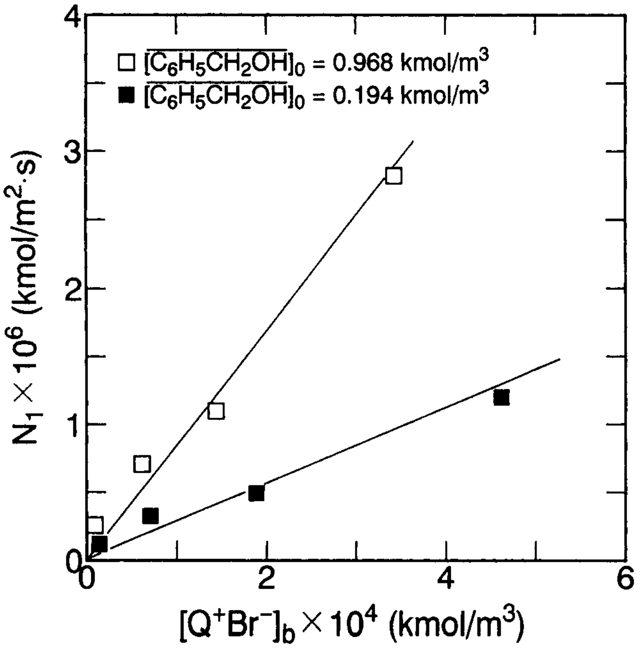

Figure 3. Effect of bulk concentration of Q^+Br^- in aqueous phase on overall reaction rates at 303 K and 0.1 kmol/m^3 OCl^- ion in aqueous phase.

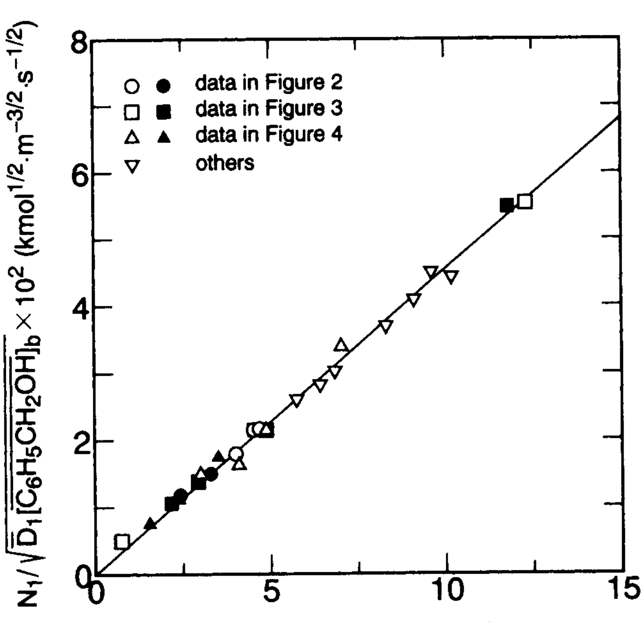

Figure 5. Determination of second-order reaction rate constant $\overline{k}$ from all experimental data at 303 K.

phase. Then, the reaction rate constant $\overline{k}$ can be determined from the slope of the straight line of the $N_1/\sqrt{\overline{D}_1\overline{[C_6H_5CH_2OH]}_b}$ vs. $\overline{[Q^+OCl^-]}_i$ plots. The plot of Eq. 28 based on the data for all runs are shown in Figure 5. All experimental values are proportional to the organic phase interfacial concentration $\overline{[Q^+OCl^-]}_i$. From the slope of the straight line, the second-order reaction rate constant $\overline{k}$ was determined to be 22.7 m^3/kmol·s at 303 K, independent of the physical properties of the aqueous solution. This value is about 10 times that of Do and Chou (1990) using 1,2-dichloromethane and tetrabutylammonium chloride as a solvent and a phase-transfer catalyst, respectively.

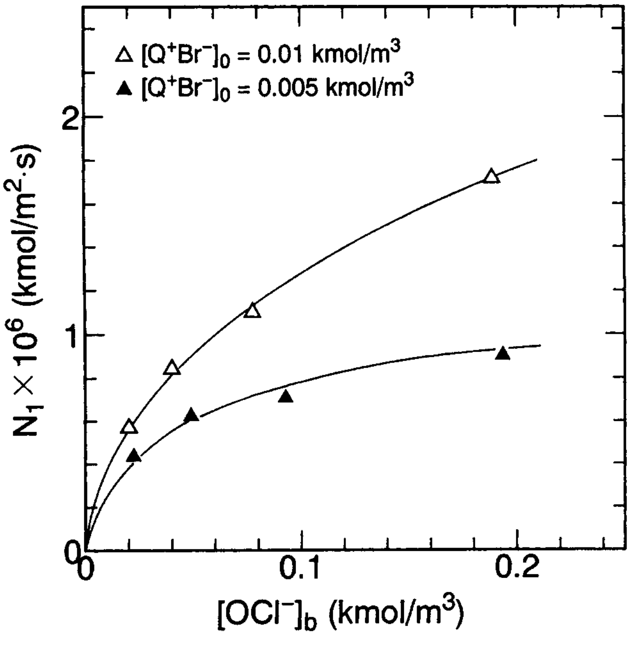

Figure 4. Effect of bulk concentration of OCl^- ion in aqueous phase on overall reaction rates at 303 K and 0.968 kmol/m^3 $C_6H_5CH_2OH$ in organic phase.

Figure 6 shows the time courses of the yields of the products,

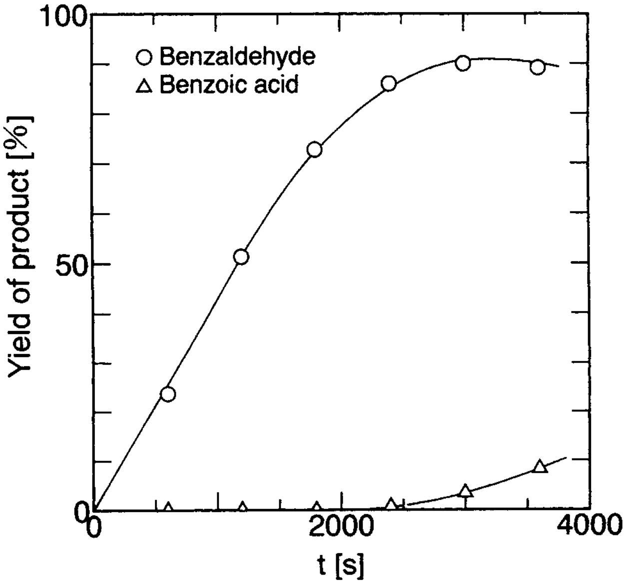

Figure 6. Time courses of yields of products at 303 K: $[Q^+Br^-]_0$ = 0.02 kmol/m^3, $[OCl^-]_0$ = 0.1 kmol/m^3 and $\overline{[C_6H_5CH_2OH]}_0$ = 0.968 kmol/m^3.

benzaldehyde and benzoic acid, for a typical run. Benzoic acid is formed by reaction:

$$\overline{Q^+OCl^-} + \overline{C_6H_5CHO} \rightarrow \overline{C_6H_5COOH} + \overline{Q^+Cl^-} \qquad (29)$$

which proceeds consecutively to the main reaction a. The yield of benzaldehyde increases greatly with time at the beginning of the run, and reaches a maximum value of 89%. On the other hand, benzoic acid is not produced at the beginning of the run, but its yield becomes about 8% at the end of the run. Namely, when the conversion of OCl^- ion in the aqueous phase is lower than 80%, the selectivity of benzaldehyde is 100%. However, at the end of the run (complete dissipation of OCl^- ion), the selectivity falls to 90% by the formation of benzoic acid. The maximum yield 89% is comparable to the previous results for the oxidation by hypochlorite in the presence of phase-transfer catalyst, that is, the 91% of Do and Chou (1990) using the above mentioned system and the 88% of Tabushi and Koga (1979) using 1,2-dichloroethane and trioctylmethylammonium chloride. However, this value is larger than that of the 76% of Lee and Freedman (1975) using 1,2-dichloroethane and tetrabutylammonium bisulphate.

Conclusion

The formation of benzaldehyde from benzyl alcohol and hypochlorite ion via phase-transfer catalysis was investigated in a heterogeneous liquid-liquid system. The phase-transfer catalyst and solvent used were cetyltrimethylammonium bromide (CTMAB; Q^+Br^-) and toluene, respectively. This reaction, which does not occur without a catalyst at ordinary temperatures and pressure, was accelerated remarkably by the addition of CTMAB even under mild conditions.

The observed reaction rates between $C_6H_5CH_2OH$ and Q^+OCl^- were proportional to the organic-phase interfacial concentration of Q^+OCl^-, which was a unique function of the concentrations of Q^+Br^- and OCl^- ion in the aqueous phase. The observed overall reaction rates were reasonably explained by the proposed analytical solution for the irreversible fast pseudo first-order reaction considering the mass-transfer resistance of the relevant reaction species.

The reaction rate constant was determined to be 22.7 $m^3/kmol \cdot s$ at 303 K, independent of the concentrations of Q^+Br^- and OCl^- ion in the aqueous phase.

The experimental results indicated that the maximum yield of benzaldehyde is about 90% and the selectivity of benzaldehyde remains 100% until the conversion of OCl^- ion in the aqueous phase reaches about 80%.

Notation

D = diffusivity, m^2/s
I = ionic strength of solution, $kmol/m^3$
$\overline{k}$ = second-order reaction rate constant, $m^3/kmol \cdot s$
$\overline{k}'$ = pseudo first-order reaction rate constant defined by Eq. 3, 1/s
k_L = mass-transfer coefficient, m/s
K = dissociation constant in aqueous phase, $kmol/m^3$
m = distribution coefficient between organic and aqueous phases,
N = mass-transfer rate, $kmol/m^2 \cdot s$
r_j = consumption rate of species j at interface, according to reactions b–d, $kmol/m^2 \cdot s$
R_j = net consumption rate of species j by reactions b–d in aqueous phase, $kmol/m^3 \cdot s$
$\overline{R}_j$ = consumption rate of species j by reaction a in organic phase $kmol/m^3 \cdot s$
Q^+ = $C_{16}H_{33}(CH_3)_3N^+$
X^- = OCl^-, Cl^-, and Br^-
z = distance from interface, m
[ ] = concentration, $kmol/m^3$

Greek letters

$\overline{\gamma}$ = dimensionless number defined by Eq. 20
δ = film thickness, m

Superscript

$\overline{}$ = organic phase

Subscripts

b = bulk
i = interface
j = species j
obs = observed
w = water
0 = initial
1 = Q^+OCl^-
2 = Q^+Cl^-
3 = Q^+Br^-
4 = OCl^-

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